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Structure sensitive adsorption of hydrogen on ruthenium and ruthenium-silver
catalysts supported on silica

by

Naresh Kumar

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Chemical Engineering
Major Professor: Prof. Terry S. King

Iowa State University
Ames, Iowa
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To My Mentors

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ABSTRACT

Supported metal catalysts typically consist of particles with sizes less than 10 nm, and because of the small crystallite size, low coordination number sites (edges and corners) represent a significant fraction of all surface sites. Furthermore, it has been demonstrated that adsorption rates can be much greater at these low coordination sites than on basal plane sites. What has not been generally appreciated, however, is that preferential adsorption at edge and corner sites may explain the mechanism by which a promoter, or the addition of a second metal to form a bimetallic, can alter the selectivity and rate of reaction. For example, our measurements of hydrogen adsorption onto supported Ru-Ag catalysts show marked decreases in the amount of hydrogen adsorbed relative to the amount adsorbed on Ru catalysts. Although it is known that Ag does not dissociatively adsorb hydrogen, this decrease cannot be explained by a simple one-to-one site blocking mechanism unless Ag preferentially populates edges and corners, thereby reducing the number of Ru edge sites. Indeed, Monte Carlo simulations of Ru-Group IB metal catalysts predict that Group IB metal atoms preferentially populate corner and edge sites of ruthenium crystals. This evidence, taken together, suggests that adsorption occurs preferentially at Ru corner and edge sites, which act as “portals” onto basal planes.

A model based on this “portal” theory for hydrogen adsorption onto supported ruthenium bimetallic catalysts has been developed using a rate equation approach. Specifically, the model accounts for the following features: (1) preferential adsorption through “portals”, (2) basal plane site-energy multiplicity, and (3) hydrogen spillover onto the support. A comparison of model predictions with experiment is presented for different concentration of Ag in Ru-Ag catalysts.

The “portal” model of hydrogen adsorption can explain the observed decreases in the amount of hydrogen adsorbed on Ru-Ag catalysts. The model can also be applied to understand the kinetics of ethane hydrogenolysis on Ru-Ag catalysts. The model is able to explain the change in the apparent order of hydrogenolysis reaction with respect to hydrogen from -1.4 to -2.4 when Ag is added to Ru/SiO₂ catalyst.

CHAPTER 1. GENERAL INTRODUCTION

Heterogeneous catalytic processes are used to create 20 % of world GNP, which is equivalent to about \$ 5 trillion per year (Lambert, 1997). Platinum group metals alone are involved in more than 25 % of the global industrial output. The major industrial applications of catalytic technology are in the areas of oil refining, petrochemicals production, and environmental protection. Most catalysts are porous with a high surface area in order to have high activity per unit weight of the catalyst. Supported bimetallic catalysts are generally used due to their higher selectivity and stability compared to monometallic catalysts. Consequently, bimetallic catalytic systems have received considerable attention from industry and academia. In the petroleum refining industry, platinum bimetallics such as Pt-Re and Pt-Ir have mostly replaced monometallic Pt reforming catalysts supported on alumina. The Pt-Rh system is used in automobile catalysts for emission control.

Considerable effort has been directed toward understanding the catalytic properties of the above bimetallic systems. As expected, their catalytic properties are related to their solid state structure. However, their structure is very complex. These highly dispersed metal catalysts are very small in size, few nanometer. A single bimetallic cluster can have as few as 200-2000 metal atoms making the task of their characterization experimentally extremely difficult. Theoretical predictions of the structure

have been made using computational techniques such as Monte Carlo simulations (Schoeb *et al.*, 1992). In Pt-Rh bimetallic, for example, the mixing of the two elements appears to be random on the surface of the particles. In addition, the surface composition of hydrogen covered Pt-Rh system has been found to be slightly enriched in Rh, which is significantly different from the surface composition of adsorbate-free surfaces which are enriched in Pt.

Understanding the alloy action of the above catalysts is difficult. The catalytic activities and selectivities of individual Group VIII elements Pt, Rh, Ir etc. can be, in many cases, comparable to each other. This makes it difficult to separate the catalytic contributions of one element from the other. The above problems can be circumvented by using a simpler bimetallic system. In recent years there has been a growing interest in understanding the action of bimetallic catalysts which are made of one Group VIII and one Group IB element. This is because they represent a much simpler system. It is expected that the main conclusions reached from the Group VIII-IB bimetallics may turn out to hold for other systems comprising a Group VIII element and a metallic element from Groups IB to IVB.

In the present work Ru and Ru-Ag bimetallic catalysts have been investigated as a model catalytic system. The interaction between Ru and Ag is much simpler compared to the complex systems such as Pt-Rh, for example. Ru and Ag metals are completely immiscible in the bulk. In spite of their

immiscibility they still form bimetallic aggregates whose surface properties reveal extensive interaction between the two elements. That they indeed form bimetallic aggregates has been shown from chemical probes such as chemisorption and reaction rate measurements, and physical probes, such as extended X-ray absorption fine structure (EXAFS) (Sinfelt *et al.*, 1980). Monte Carlo atomistic simulations have shown that when Ag is added to the Ru particles it segregates to the surface and on the surface silver atoms preferentially populate edge and corner sites of Ru-Ag bimetallic crystallites (Smale and King, 1990). As the concentration of Ag is increased, basal planes get progressively populated with Ag atoms. Experiments carrying out deposition of Ag atoms on single crystal Ru surfaces show further evidence that Ag atoms prefer low coordination number sites (Schick *et al.*, 1994).

Ruthenium metal can be used as a catalyst for industrially important reactions such as Fischer-Tropsch synthesis and ammonia synthesis. Catalysts based on Ru and using alkali as promoters are expected to become the second generation ammonia synthesis catalysts (Tennison, 1991). Promoted Ru catalysts supported on carbon have been used in a 600 MTPD NH_3 plant which started production in 1992 (Czuppon *et al.*, 1993). The operating temperature and pressure for the Ru-based catalysts are lower compared with the synthesis processes which use the traditional magnetite-based systems. The ammonia synthesis pressure is 70 - 105 bar compared

with 150 - 300 bar in the processes with conventional catalysts and also the Ru catalysts lead to a higher conversion. Fischer-Tropsch synthesis can be broadly defined as the reductive polymerization of CO by H₂ to form organic products containing primarily carbon and hydrogen (Satterfield, 1991). The selectivity of the Ru catalysts in Fischer-Tropsch synthesis reactions can be improved by adding promoters such as potassium.

Hydrogen is involved as a reactant or as a product in not only Fischer-Tropsch and ammonia synthesis reactions but also many other industrially important reactions such as catalytic reforming of petroleum feedstock, hydrocracking, and hydrogenation of unsaturated fatty acids. Most of these catalytic reactions are structure sensitive. A catalytic reaction is structure sensitive if the reaction rate depends on the detailed geometrical structure of the surface atoms of the metal particle (Boudart, 1969). Some of the structure sensitive and structure insensitive reactions have been listed in Appendix C.

Most metallic catalysts need to be reduced before they can be used. These catalysts are mostly reduced by hydrogen. The catalytic behavior can itself be influenced by the reduction conditions (Burch, 1988). Hydrogen chemisorption on supported metal catalysts is also used to characterize the active sites on the surface of the metal particles. The number of metal atoms on the surface of metal particles which is used in calculating dispersion is usually determined by hydrogen adsorption and assuming hydrogen-to-metal stoichiometry. Hydrogen adsorption is strongly affected by the heterogeneity

of the metal surface. Low coordination number sites such as edges and corners of the metal particle, crystallographic defects or impurity atoms can drastically affect the rate of hydrogen adsorption on the surface of the metallic catalysts.

Chemisorption of a gas on the solid catalyst constitutes the first step in a heterogeneously catalyzed reaction. This process of gas adsorption on the surface of the catalyst may itself be structure sensitive. Interactions of hydrogen with many metal catalysts have been found to be a structure sensitive process.

Most of the fundamental investigations on the hydrogen-metal systems have been carried out on single crystals under ultra high vacuum conditions. In industry the catalysts used are highly dispersed on supports like silica, alumina or zeolites and are used under much higher pressure. In practice the catalytic systems contain more than one element in order to improve selectivity towards a desired product and stability of the catalyst. Such multicomponent catalysts are difficult to study due to their complex structure and catalytic effects. Investigation into the behavior of bimetallic catalysts constitutes a first step in understanding multicomponent catalysts.

The pioneering work on bimetallic catalysts was carried out by Sinfelt (1983). The highly dispersed entities on the surface of supports such as silica or alumina were referred to as bimetallic clusters rather than highly dispersed alloys. Many bimetallic systems are immiscible in the bulk but show catalytic effects as if they are working in tandem when highly dispersed on a support.

Significant changes in activity and selectivity have been noted on addition of a second metal to metallic catalysts (Ponec and Sachtler, 1972; Sinfelt, 1973; Clarke, 1975; Ponec, 1983; Campbell, 1990).

Supported metal catalysts typically consist of particles with sizes less than 10 nm. Surfaces of such small particles are extremely difficult to be fully characterized by currently available experimental techniques. Therefore, several different approaches have been used to try and predict surface composition of bimetallic particles. In binary systems one element tends to be present at the surface in a concentration greater than it exists in the bulk. This surface segregation can also be a function of the gases interacting with the surface of the particle.

Surface structure of hydrogen-metal systems can be determined by using LEED or ion channeling techniques when the catalysts are in the form of a single crystal. HREELS (high resolution electron energy loss spectroscopy) can probe the local geometry of adsorption sites. Measurements using the above techniques have revealed that hydrogen occupies the fourfold hollow sites on Ni(100) (Andersson, 1978) and on Pd(100) (Nyberg, 1983). Hydrogen was located at threefold hollow sites on Ni(111) (Ibach, 1980) and on Ru(0001) (Conrad *et al.*, 1983; Barteau *et al.*, 1983). Hydrogen atoms have also been determined to occupy twofold bridge sites on W(100) (Barnes *et al.*, 1978).

The interaction of hydrogen with single crystal surfaces under ultra high vacuum conditions cannot always be extrapolated to high pressure conditions for highly dispersed catalytic systems. At elevated pressures adsorbed hydrogen may exist in the form of weakly bound species and can play a significant role in catalytic reactions. The presence of low coordination number sites such as edges and corners of the highly dispersed metal particles is believed to play an important role in interaction of these species with the surface of the metal particles.

Due to the small size of the metal crystallites a large number of metal atoms lie on the surface of the particles and take part in the catalytic reaction. In nanosize particles low coordination number sites such as edges and corners represent a significant fraction of all surface sites. Single crystal studies have demonstrated that adsorption rates can be much greater at these low coordination sites than on basal plane sites. What has not been generally appreciated, however, is that preferential adsorption at edge and corner sites may explain the mechanism by which a promoter, or the addition of a second metal to form a bimetallic, can alter the selectivity and rate of reaction. For example, our measurements of hydrogen adsorption onto supported Ru-Ag catalysts show marked decreases in the amount of hydrogen adsorbed relative to the amount adsorbed on Ru catalysts. Although it is known that Ag does not dissociatively adsorb hydrogen, this decrease cannot be explained by a simple one-to-one site blocking mechanism unless Ag preferentially populates

edges and corners, thereby reducing the number of Ru edge sites. Indeed, Monte Carlo simulations of Ru-Group IB metal catalysts predict that Group IB metal atoms preferentially populate corner and edge sites of ruthenium crystals (Smale and King, 1990). This evidence taken together, suggests that adsorption occurs preferentially at Ru corner and edge sites, which act as *portals* onto basal planes.

The work presented in this dissertation is aimed at addressing the role of low coordination sites in adsorption of hydrogen on Ru/SiO₂ and Ru-Ag/SiO₂ systems. A “portal” theory for hydrogen adsorption on ruthenium bimetallic catalysts is developed using a rate equation approach. This theory explains how addition of Ag to Ru/SiO₂ drastically reduces the hydrogen adsorption amount per Ru atom. The theory is also used to explain the change in the apparent order of hydrogenolysis reaction with respect to hydrogen. The reaction order with respect to hydrogen changes from -1.4 to -2.4 when almost all the low coordination sites of Ru particles of Ru/SiO₂ are populated by Ag atoms.

Dissertation Organization

This dissertation has been organized into five chapters. Chapter 1 contains General Introduction and the Literature Review is presented in Chapter 2. Chapter 3 and Chapter 4 each correspond to a paper written in a

format suitable for publication in a technical journal. They represent original work carried out by the author. In Chapter 3 the interaction of hydrogen with Ru/SiO₂ and Ru-Ag/SiO₂ is investigated and is explained by a new model called *portal model* of adsorption. This paper is to be submitted to the journal *Chemical Engineering Science*. In Chapter 4, the change in negative order of Ethane Hydrogenolysis reaction with respect to the partial pressure of hydrogen on Ru and Ru-Ag catalysts is explained. In this analysis the portal model of hydrogen adsorption is used. This paper is to be submitted to the journal *Catalysis Letters*. The General Conclusions which also contain recommendations for future work are presented in Chapter 5. In Appendix A the derivation of the model equations is presented. The schematic of the experimental setup is shown in Appendix B. A list of structure sensitive and structure insensitive reactions is tabulated in Appendix C. References cited in Chapters 1, 2 and 5 are listed following the appendices.

CHAPTER 2. LITERATURE REVIEW

Supported bimetallic catalysts are generally used in heterogeneous catalysis due to their higher selectivity and stability as compared to the monometallic catalysts. Consequently bimetallic catalytic systems have received considerable attention from industry and academia. In petroleum refining industry platinum bimetallics like Pt-Re and Pt-Ir have mostly replaced the monometallic Pt reforming catalyst supported on alumina. Pt-Rh system is used in automobile catalysts for emission control.

The behavior of the above bimetallics can be better understood by looking into model catalytic systems. Individual metals from Groups VIII and IB of the periodic table are used for such model systems. Sinfelt (1983) has considered some of the features characteristic of hydrocarbon reactions on catalysts containing Ag, Au or Cu. In the present work Ru-Ag bimetallic supported on silica was considered for hydrogen adsorption study. Ruthenium has received considerable attention in the laboratory and plant studies for Fischer-Tropsch synthesis and ammonia synthesis. Fischer-Tropsch catalysts contain a small amount of potassium which acts as a promoter (Satterfield, 1991).

The metallic catalysts can exist in the form of bulk metal or in a dispersed state on a nonmetallic support. Some of the oxides which are used as support are alumina, silica, zeolite, titania, magnesia, and carbon. These

supports have a high surface area and help metals in having a high specific surface area since the catalytic phenomena occur at the surface of the metal particles. The surface area of the metal is generally expressed in terms of dispersion which is defined as the ratio of the number of surface metal atoms to the total number of metal atoms in the sample (Boudart, 1969, 1984). The dispersion of a catalyst is related to the particle size and surface area of the metal particles in the sample. Supports prevent the growth of the metal particles by coalescence during the use and regeneration of the catalytic samples.

Determination of the size of the metal nanoparticles is difficult by physical techniques such as X-ray diffraction line broadening and electron microscopy. Since the percent of atoms exposed is the most pertinent from the viewpoint of catalysis, dispersion is usually measured by selective chemisorption of gases such as H_2 and CO. As a good approximation for the transition metal with particles of spherical shape, the dispersion D and particle size d are related by $D \approx 0.9/d$, where D is expressed as ratio and d is in nm (Boudart, 1975, 1984). From the above expression it can be seen that a dispersion range of 20 to 30 % corresponds to an average particle size of 4.5 - 3 nm. Structure and properties of such small metal particles have been reviewed in the literature by several authors (Anderson, 1975; Hayward and Trapnell, 1964; Poltorak *et al.*, 1971).

The final shape of the above nanosize particles is governed by the kinetic and thermodynamic factors. The equilibrium shape can be constructed by applying the principles of Wulff theorem. The shape and structure of small ruthenium metal crystallites on model oxide surfaces have been investigated using transmission electron microscopy (Datye, 1988). The electron micrographs of the Ru crystallites on silica and magnesia showed the small crystallites to be spherical and the larger crystallites appeared to have characteristic ellipsoidal shapes. The larger crystallites were faceted and exposed the $\{0001\}$, $\{10\bar{1}1\}$, and $\{10\bar{1}0\}$ surfaces of ruthenium. Here, it should be mentioned that the support and the precursors used were different from the ones used in the present work. In another investigation, ruthenium and ruthenium-copper bimetallic catalysts were studied by electron microscopy (Prestridge *et al.*, 1977). The average diameter of the clusters was found to be less than 5 nm. The bimetallic ruthenium-copper clusters were believed to have a raft like structure visualized as a layer of ruthenium atoms covered by copper atoms. In some cases, some of the larger particles appeared to have a three dimensional structure rather than two dimensional form of the raft-like clusters.

The size of metal particles affect the activity and selectivity of heterogeneous catalysts. A reaction is characterized to be structure-sensitive if its turnover frequency varies with the size of the catalytic metal particles

(Boudart, 1969). A change in the size of the metal particle varies the relative proportion of atoms on the edges and corners, which have low coordination numbers, and on the basal planes. Experimentally it is extremely difficult, if not impossible, to quantify the number of atoms which lie on low coordination number sites and on basal planes. This can be overcome by assuming that the metal particles take shapes of cubo-octahedra or other symmetric geometric shapes. Schematic of a cubo-octahedron is shown in Figure 1.

van Hardeveld and Hartog (1969) assumed that the maximum stability of the small crystals corresponds to the lowest possible number of free valences on the surface and concluded that the most stable shape of particles containing 600-700 atoms is spherical. The electron micrographs of Pt and Pd metal particles indicate a near spherical shape with 1.5-2.5 nm diameter.

Some researchers believe that the equilibrium shape of the FCC nanocrystals of the supported metal catalysts can be represented by octahedral and cubo-octahedral shapes (Poltorak *et al.*, 1971; Bond, 1971). Poltorak has proposed that the stable shape of particles 2.0-2.5 nm in diameter is octahedral and cubo-octahedral if the particles are larger than 3.0 nm. From such geometry the relative number of atoms with different coordination numbers can be determined. The relative number of atoms with low coordination numbers increases when the total number of atoms in the particle decreases with a decrease in the particle size. The structural properties of

octahedra and cubo-octahedra of varying sizes and the proportion of surface atoms with different coordination numbers can be found in the literature (Anderson, 1975; Kiselev and Krylov, 1989). The above models of octahedra and cubo-octahedra represent the complete crystals. However, the small crystallites can also occur in an incomplete form if the number of metal atoms is less than the requisite number.

From an earlier work in our group atomistic simulations were performed for perfect cubo-octahedral structures (Strohl and King, 1989). From the statistics of atoms with different coordination numbers, it has been found that the fraction of atoms with low coordination number (y_p) can be related to the dispersion (D , expressed as ratio) by the following expression: $y_p = 0.882 D - 0.023$, where dispersion is between 0.1 and 0.6. The remaining part of the fraction corresponds to the atoms lying on the basal planes of the nanocrystal.

Investigations of bimetallic catalysts were inspired by the observation that the incorporation of Group IB metal with a Group VIII markedly decreases the activity of the Group VIII metal for hydrogenolysis of hydrocarbons (Sinfelt, 1983). Compared to Group VIII metal the hydrogenolysis activity of Group IB metal is negligible. Inhibition of hydrogenolysis results in increased selectivity for the desired reactions such as hydrogenation, dehydrogenation, isomerization, or aromatization. The above

behavior has been shown by Ru-Ag and Ru-Cu bimetallic catalysts for the conversion of cyclohexane to benzene (Sinfelt *et al.*, 1971).

The structure of a bimetallic catalyst whose both elements are from Group VIII can be very complicated and is too complex to render any physical insight. For example, Figure 2 shows the configuration of Pt and Rh atoms of a Pt-Rh bimetallic system obtained from Monte Carlo simulation. The mixing of two metal appears to be random. Bimetallic catalysts of Group VIII and IB metals show much simpler features. Figure 3 shows the surface of a Ru-Cu metal particle and the preferential occupation of edges and corners of the particle by Cu atoms is evident.

The structure of Ru-Ag bimetallic system has been investigated by atomistic simulations (Strohl and King, 1989; Smale and King, 1990). Supported Ru-Ag bimetallic system was modeled with a Monte Carlo simulation technique using a coordination dependent potential model and its structure is presented in Figure 4. Cubo-octahedral particles with dispersions in the range of 30 % to 60 % range were studied. From the simulations it was observed that when a small amount of Ag was added to a ruthenium metal particle, silver atoms preferentially populated the edge and corner sites of the bimetallic crystallites. At higher content of silver the low index planes were covered with silver. Ru-Ag system required higher amount of the Group IB metal before there was no longer any ruthenium at the edge and corner sites

of the metal particles than was required in the case of Ru-Cu bimetallic system.

Silica supported Ru-Ag bimetallic system has been studied by hydrogen chemisorption and by nuclear magnetic resonance, NMR (Wu *et al.*, 1990). From the ^1H NMR studies it was concluded that at higher silver contents two and three dimensional Ag islands were formed on Ru particles with essentially no mixing of silver and ruthenium atoms on the surface planes.

The edges and corners of the supported metal particles have low coordination numbers. The characteristics of these sites are expected to be similar to that of step sites on the surface of a single crystal. The catalytic activities of these step sites have been extensively characterized in many single crystal studies carried out under ultra high vacuum (Bernasek and Somorjai, 1975; Christmann and Ertl, 1976). Bernasek and Somorjai (1975) have studied the hydrogen-deuterium exchange reaction by molecular beam scattering on low and high Miller index crystal faces of platinum single crystal. Three platinum single crystal surfaces used were designated by Miller indices as Pt(111), Pt(997) and Pt(553) surfaces. These planes were used for $\text{H}_2\text{-D}_2$ exchange reactions which were generally performed by scattering a deuterium beam from the Pt surface in an ambient of hydrogen. The low index Pt(111) surface did not produce a significant amount of HD whereas the stepped Pt surfaces (997) and (553) were approximately 100 times more active

for hydrogen-deuterium exchange than Pt(111) surface. The activity of the higher step density surface Pt(553) was about twice of the lower step density surface Pt(997).

Gale *et al.* (1977) have looked into the variation of surface reaction probability with reactant angle of incidence for the above system. On the steps of a high Miller index surface, Pt(332), a marked increase in the production of HD was observed when the molecular beam hit the open side of the step structure. On the smooth Pt(111) surface, a smooth decrease in HD production was observed when the incidence angle of the molecular beam was changed from normal incidence to grazing angles. The effect of incidence angle and azimuthal angle with the surface of Pt single crystal surface on its activity is shown in Appendix D.

Smith *et al.* (1988) have also proposed that the edge sites are more active for dissociative adsorption of hydrogen on supported Pd and Pt catalysts. Schick *et al.* (1994) have studied the growth of silver film on substrates like single crystal ruthenium. The growth of Ag films was studied on a flat Ru(0001) surface as well as on a stepped Ru($10\bar{1}17$) surface. The adsorption of Ag on the ruthenium surface was studied using the techniques of TDS (thermal desorption spectroscopy), AES (auger electron spectroscopy), LEED (low energy electron diffraction), ARUPS (angle resolved photoelectron spectroscopy) and PAX (photoemission of adsorbed xenon). It was observed

that Ag atoms adsorb preferentially at the step sites of the Ru(10 $\bar{1}$ 17) surface. Selective initial population of the Ru step sites was completed at about the ideally required 0.12 ML of Ag atoms to decorate all step sites of the stepped Ru surface. At higher coverages Ag atoms formed islands on the surface of the ruthenium crystal. On flat Ru(0001) surface two-dimensional Ag islands were formed from a very low Ag coverage of 0.05 ML.

Hydrogen can exist in various states on the surface of metal particles due to the heterogeneity of the surface of the crystallites. Hydrogen adsorption on Ru/SiO₂ has been investigated by NMR to determine this (Bhatia *et al.*, 1994). Two peaks were observed and were termed as α and β . The hydrogen species represented by α peak corresponded to a strongly bound hydrogen on the surface of Ru metal particles. The adsorbed hydrogen was believed to occupy the three-fold hollow sites. The exact nature of the adsorbed hydrogen species represented by β species is not very clear. It can be thought to be a weakly bound species of adsorbed hydrogen as it appears only when the gas phase pressure of H₂ was above 100 Torr. The heat of adsorption from microcalorimetry for α species was determined to be about 70 kJ/mol while the heat of adsorption of β species was found to be very low at 10 kJ/mol. Metal particles with higher dispersion were found to have larger amount of weakly adsorbed β species.

The dynamics and energetics of hydrogen chemisorption on silica supported ruthenium and ruthenium-silver bimetallic catalysts have also been investigated by ^1H NMR spectroscopy and microcalorimetry (Savargaonkar *et al.*, 1998). The amount of hydrogen adsorbed on Ru particles was drastically reduced with addition of silver. The increasing amounts of silver also led to depopulation of adsorbed hydrogen species having intermediate and low heats of adsorption.

The weakly bound hydrogen species is very mobile on the surface of the metal particle. These mobile species can move from the metal particles to the surface of the oxide on which the metal particles are supported. This phenomenon has been termed as spillover. Any hydrogen chemisorption measurement must also take into account the spillover as in some cases the amount of spillover hydrogen can be significant compared to the adsorbed species on the metal particles. The diffusion and desorption of spillover hydrogen on various support surfaces have been considered in literature.

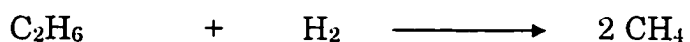
Robell *et al.* (1964) have studied surface diffusion of hydrogen on platinized carbon. Hydrogen, after adsorption on Pt sites, was found to migrate to the support. It was observed that hydrogen molecules adsorbed rapidly on platinum sites and then spilled over to the support by an activated slow process of surface diffusion. The platinum-carbon system was assumed to consist of platinum centers surrounded by carbon centers. Platinum centers

were equilibrated adsorption zones which acted as the source for surface diffusion of hydrogen on the carbon support. The surface diffusion was found to be activated and the activation energy was estimated to be as high as 39.2 kcal/mol. The diffusion coefficient of hydrogen species on carbon support was determined to be 3.4×10^{-19} cm²/s at 300 °C and 5.8×10^{-17} cm²/s at 392 °C.

Fleisch and Abermann (1977) have investigated the diffusion of hydrogen from Pt to a Ag₂S phase boundary by following the reduction of a thin Ag₂S film which was either in direct contact with a Pt film or separated from Pt film by carbon or SiO. The thin films of SiO, Ag₂S and Pt were deposited on MgO which was on a freshly cleaved mica sheet. The Pt films acted as a source of hydrogen while Ag₂S layer acted as a sink as it was reduced to Ag. In the specimen used to investigate the diffusion of hydrogen the source and sink were separated by the support. As Ag₂S film was reduced by hydrogen dissociatively adsorbed on Pt film and spilled over the support to the Ag₂S. The dependence of the width of the gap between Pt and Ag₂S with reduction time was monitored. The diffusion of reactive hydrogen from the Pt surface over the support to the Ag₂S phase boundary was determined to be the rate-determining step. From the electron microscopic observation of the specimen hydrogen was found to diffuse over distances of the order of 200 nm. The diffusion coefficients were found to be 5.3×10^{-14} cm²/s at 100 °C and 1.5×10^{-11} cm²/s at 200 °C. The activation energy for the surface diffusion was found

to be 15.5 kcal/mol. Associative desorption of hydrogen from the surface of the support to the gas phase was not considered.

Hydrogen adsorption on the surface of Ru-Ag bimetallics supported on SiO₂ have been found to be a structure sensitive process (Savargaonkar *et al.*, 1998). One of the hydrocarbon reactions which has been found to be strongly structure sensitive is hydrogenolysis. Hydrogenolysis involves the rupture of carbon-carbon bonds and the subsequent formation of carbon-hydrogen bonds. Hydrogenolysis reactions of hydrocarbons on metals exhibit a large range of variation in rate per surface atom from one metal to another. When compared with hydrogenolysis reactions, hydrogenation and dehydrogenation of hydrocarbons show much smaller changes in rate from one metal to another. For example, rates of ethane hydrogenolysis can vary by eight orders of magnitude among the Group VIII metals (Sinfelt, 1973 a; 1974) while the rates of hydrogenation reactions such as hydrogenation of benzene to cyclohexane and of ethylene to ethane vary by only two to three orders of magnitude (Schuit and van Reijen, 1958). The simplest hydrogenolysis reaction of a hydrocarbon can be represented by conversion of ethane to methane.



Group VIII elements possess high catalytic activities for ethane hydrogenolysis reactions. However, Group IB metals are much less active

than the least active of the Group VIII metals (Sinfelt, 1983). Many heterogeneous catalytic reactions including hydrogenolysis, isomerization and deuterium exchange reactions exhibit a negative-pressure dependency on the partial pressure of one of the reactants. Ru-Ag bimetallic catalysts have been used for studying ethane hydrogenolysis reactions (Smale and King, 1990). The apparent order of reaction with respect to hydrogen for Ru/SiO₂ was found to be -1.4 while the order with respect to ethane was about 0.9. However the apparent order of ethane hydrogenolysis with respect to hydrogen was found to be more negative when 40 at % Ag was added to Ru/SiO₂. The reaction order became -2.4 from -1.4 on addition of Ag. The order with respect to ethane was unchanged. The effect of temperature on the rate and the apparent order of reaction with respect to two reactants were also determined.

In the present work the structure sensitive interaction of hydrogen with Ru and Ru-Ag catalysts supported on silica has been investigated. In the literature various adsorption models have been proposed. The first adsorption model was established by Langmuir (1918) and is still widely used. Other adsorption isotherms such as Freundlich adsorption isotherm, Tempkin adsorption isotherm, Fowler-Guggenheim isotherm have been proposed. Different aspects of gas-solid interactions and the resulting adsorption isotherms have been reviewed by Doraiswamy (1991).

Interaction of hydrogen with supported metal catalysts can be suitably probed with NMR techniques. For example, Engelke *et al.* (1994) have proposed a model which relates hydrogen mobility as observed by NMR line shapes to desorption and adsorption processes on the surfaces of the metal particles. A transition from inhomogeneous to homogeneous broadening occurred due to an increase of interparticle motion of hydrogen. A rate parameter was obtained from comparing the model with the hole burning of the inhomogeneous line shape from NMR. This rate parameter could be interpreted in terms of desorption and readsorption kinetics. Savargaonkar *et al.* (1998) have used this model to estimate apparent rate constants for hydrogen adsorption and desorption on Ru/SiO₂ and Ru-Ag/SiO₂ catalysts.

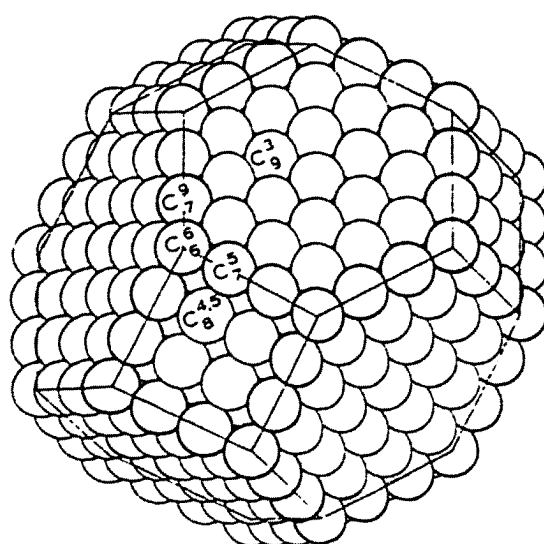
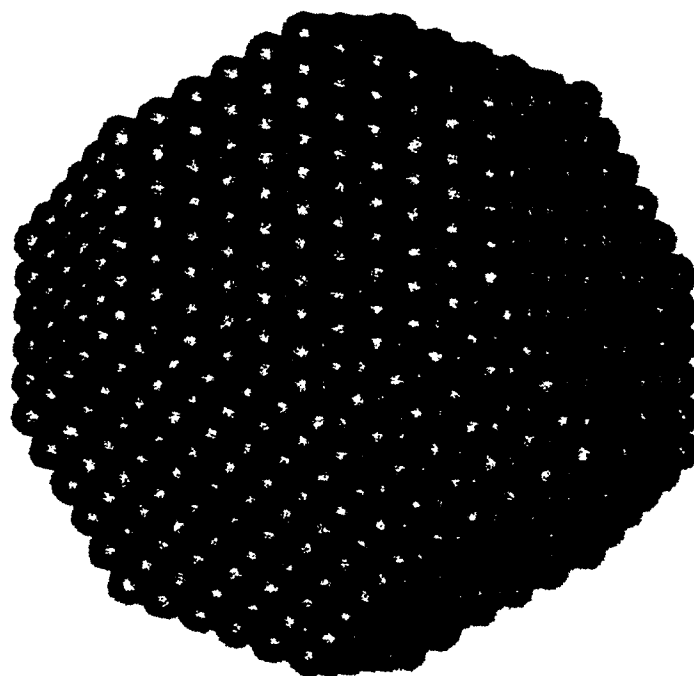


Figure 1. Schematic of a Cubo-octahedron

(a) 30 % Pt - Rh



(b) 15 % Pt - Rh

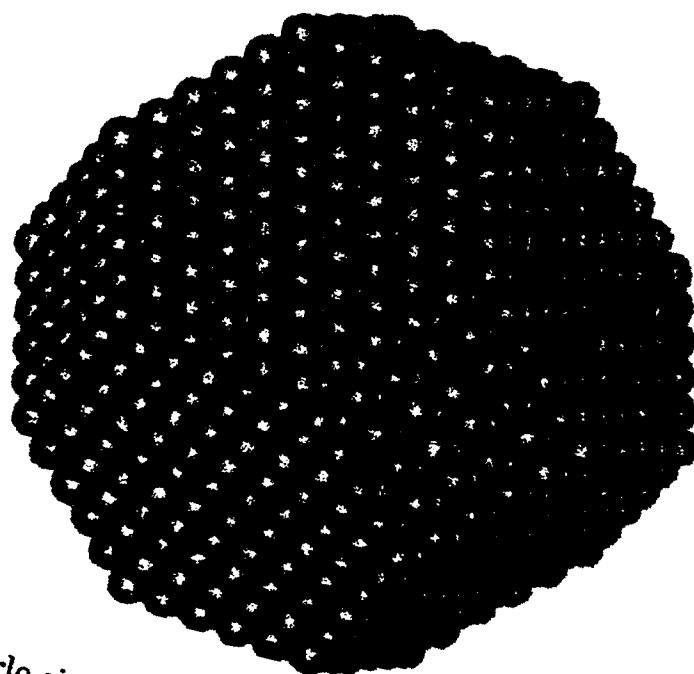
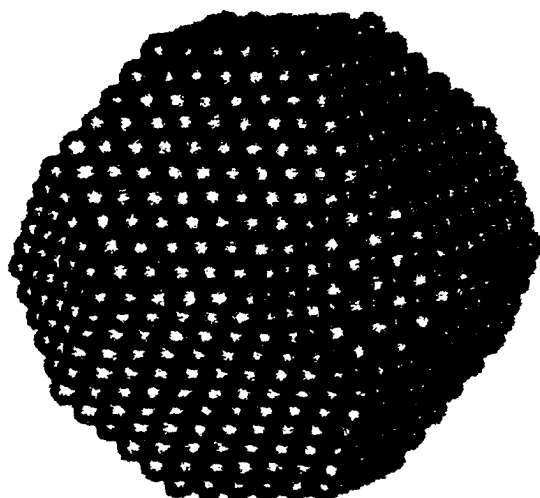
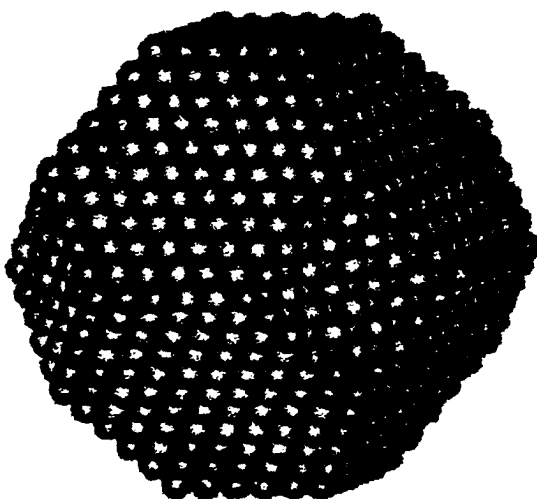


Figure 2. Monte Carlo simulations of Pt-Rh bimetallic structure with total dispersion of 31 %. Pt atoms are shown in red (dark).

(a) 5 % Cu - Ru



(b) 10 % Cu - Ru



(c) 15 % Cu - Ru

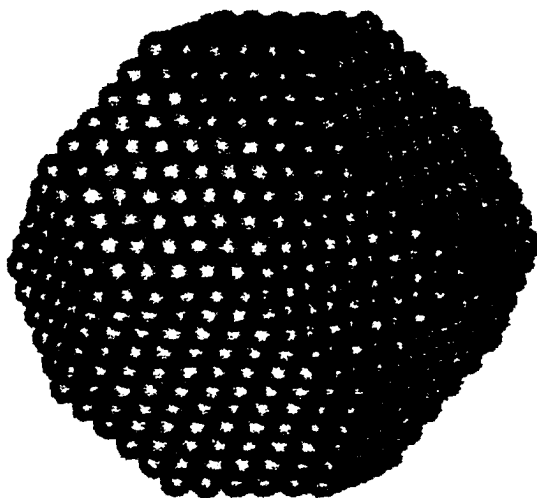


Figure 3. Monte Carlo simulations of Cu-Ru bimetallic structure with total dispersion of 31 %. Cu atoms are shown in blue (light).

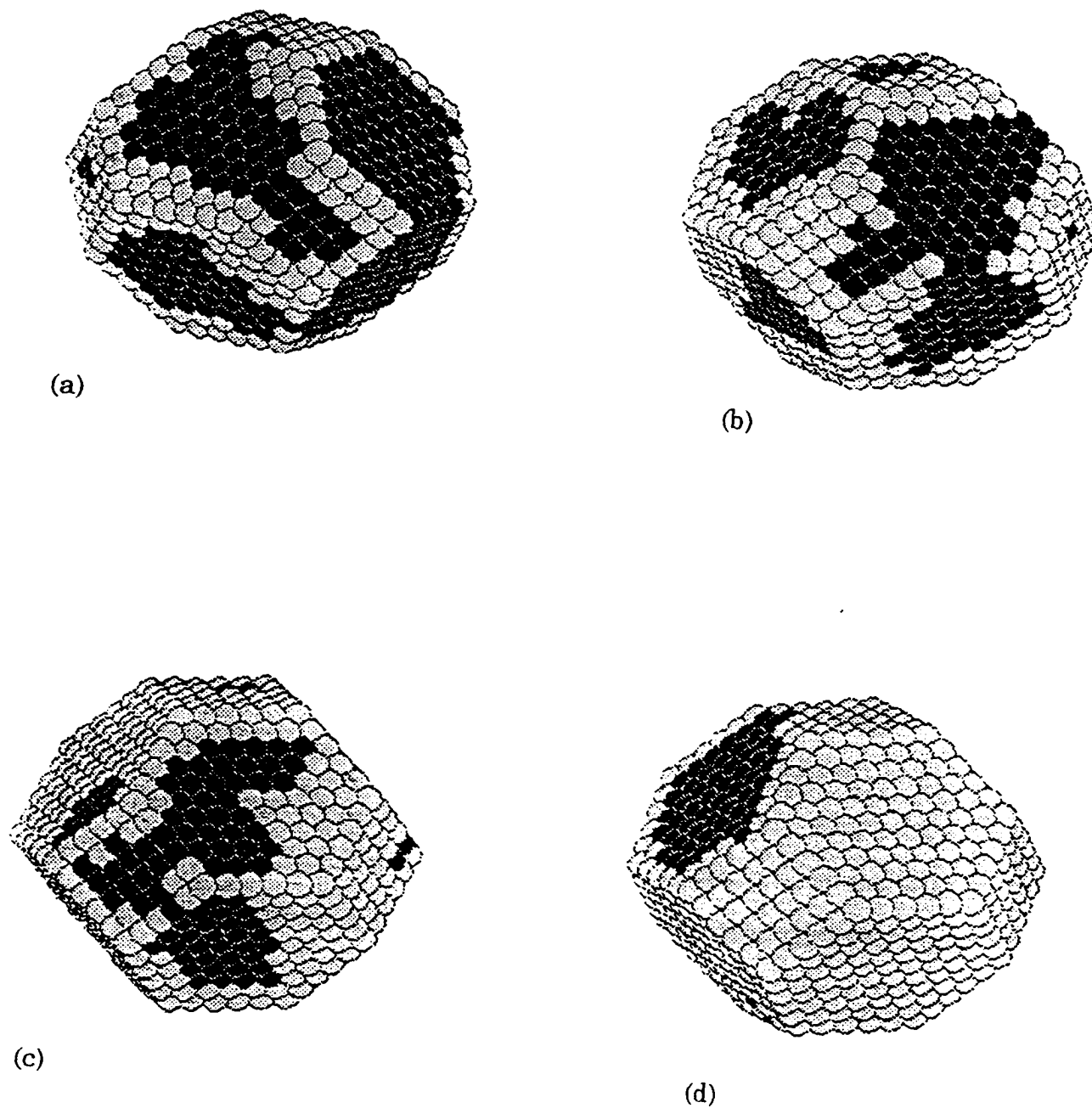


Figure 4. Monte Carlo simulation results for Ru-Ag/SiO₂ catalysts with a total dispersion of 30 %: (a) 13 % Ag, (b) 20 % Ag, (c) 30 % Ag and (d) 40 % Ag. Silver atoms are shown in light gray. (Smale and King, 1990).

CHAPTER 3. STRUCTURE SENSITIVE HYDROGEN ADSORPTION ON Ru/SiO₂ AND Ru-Ag/SiO₂ CATALYSTS: THEORY AND EXPERIMENT

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Abstract

Preferential adsorption of gases onto metal surfaces through low coordination defect, edge, and corner sites has been well documented. What has not been generally appreciated, however, is that promoter, or the addition of a second metal, can alter the selectivity and rate of reaction on supported catalysts. We propose a new model for H₂ adsorption onto supported Ru catalysts that explicitly accounts for preferential adsorption through low coordination sites, and we show that the model can explain observed decreases in the amount of H₂ adsorbed onto Ru-Ag catalysts.

Introduction

Supported metal catalysts typically consist of particles with sizes less than 10 nm. A significant fraction of surface atoms in such small crystallites occupy low coordination edge, corner, step, and kink sites, and this fraction

changes drastically with the size of the metal particle. Furthermore, because adsorption/desorption rates can be much greater at edge, corner, and defect sites than on basal plane sites, the rate of an adsorption process can depend on the density of low coordination surface sites (Bernasek and Somorjai, 1975; Christmann *et al.*, 1975; Gale *et al.*, 1977; Salmeron *et al.*, 1977; Poelsema *et al.*, 1977, 1985; Karner *et al.*, 1985; Rendulic *et al.*, 1987).

Ruthenium and silver are almost completely immiscible in the bulk (Moffat, 1988), and the heat of mixing for a Ru-Ag system is positive (92 kJ/mol of Ag) (Miedema *et al.*, 1980; Buchgeister *et al.*, 1988). Therefore, when a small amount of Ag is added to Ru, the solute segregates on the surface of the Ru particle. Atomistic simulations predict that silver atoms preferentially populate surface edge and corner sites of Ru-Ag bimetallic crystallites (Smale and King, 1990). As the concentration of Ag is increased, basal planes progressively populate with Ag. Further evidence that Ag atoms prefer low-coordination sites is provided by Ag deposition experiments on single crystal Ru surfaces. The latter experiments show that Ag atoms preferentially occupy step sites of the Ru surface and at higher coverage form two-dimensional Ag islands (Schick *et al.*, 1994).

Besides the surface segregation effects described above, the addition of Ag to Ru/SiO₂ results in a large decrease in the amount of hydrogen adsorbed per surface Ru atom (Savargaonkar and King, 1998). Microcalorimetry has

shown that this decrease is mainly associated with hydrogen atoms that have intermediate and low heats of adsorption (Narayan, 1997). There are at least four possible explanations for the decrease in the coverage of hydrogen on Ru-Ag/SiO₂ when compared to Ru/SiO₂ : (i) site blocking by silver atoms, (ii) ensemble effects that change the nature of a multiple adsorption site, (iii) electronic interactions between Ru and Ag atoms that affect the hydrogen binding to the surface Ru, and (iv) changes in the kinetics of hydrogen adsorption on Ru surfaces due to structure sensitivity.

It is possible that edge, corner and other low coordination sites of the Ru metal particles bind hydrogen atoms with intermediate and low energy of adsorption. If such sites are blocked by Ag atoms, this would explain the depopulation of hydrogen atoms with intermediate and low heats of adsorption observed by microcalorimetry (Narayan, 1997). However, sites with low coordination number form only 10-20% of the total surface atoms of a metal particle if the dispersion of Ru metal in the catalyst is in the typical range of 20 to 30%. Therefore, simple one to one site blocking cannot account for the relatively large reduction in H/Ru_{surface} unless each edge and corner Ru atom accommodates 12 to 20 hydrogen atoms, which is highly improbable. Ensemble effects also cannot explain the observed drop in adsorbed hydrogen since the Ru-Ag bimetallic system does not exhibit micromixing. Furthermore, the drop in hydrogen coverage of Ru-Ag bimetallics cannot be due to electronic interactions between Ru and Ag since ¹H NMR line shifts of hydrogen on Ru in

Ru-Ag/SiO₂ are the same as the shifts observed in Ru/SiO₂ catalysts (Savargaonkar and King, 1998). Any electronic interaction between Ru-Ag can also be expected to affect the heat of adsorption at low hydrogen coverages where adsorbate-adsorbate interactions are negligible. However, microcalorimetry has shown that the initial and low coverage heats of adsorption are similar for Ru/SiO₂ and Ru-Ag/SiO₂ catalysts (Narayan, 1997).

Based upon the above considerations, we conclude that silver probably changes the kinetics of hydrogen adsorption by preferentially occupying low coordination sites of the metal particles. In particular, we postulate that Ruthenium edge and corner sites act as gateways or “portals” through which hydrogen dissociatively adsorbs onto vacant basal plane sites. When the “portals” are blocked by Ag atoms, the result is a drastic decrease in the amount of hydrogen adsorbed. In this paper we develop a rate equation model based upon the portal hypothesis and we compare it with data collected from hydrogen adsorption experiments on Ru-Ag/SiO₂.

Model Equations

Before presenting the model equations, we briefly enumerate the key assumptions:

1. Hydrogen adsorption largely occurs through portal sites (edges and corners) at a rate independent of the hydrogen coverage on the metal.

2. Dissociated hydrogen adsorbing through portal sites immediately moves to basal plane sites.
3. In order to reduce the mathematical complexity of the model, basal plane hydrogen binding site multiplicity is reduced to two types: strong binding and weak binding sites.
4. No hydrogen is directly adsorbed from the gas phase onto weak binding sites; weak sites are populated only by hydrogen that first enters through portal sites.
5. In contrast to weak binding sites, hydrogen can dissociatively adsorb directly from the gas onto adjacent strong binding adsorption sites without passing through portal sites. This feature of the model accounts for the fact that some hydrogen does adsorb onto Ru-Ag/SiO₂ even for concentrations of silver that are sufficiently high to block all portal sites.
6. Weakly bound hydrogen can move to fill vacant strong binding sites.
7. Two weakly or two strongly bound adjacent hydrogen atoms can desorb associatively.
8. A weakly bound hydrogen atom can associatively desorb with a strongly bound hydrogen.
9. Weakly bound hydrogen atoms can spillover from metal particles to the support. The spillover process is assumed to be irreversible and first order in the coverage of weakly bound hydrogen.

The above assumptions lead to the following dimensionless rate equations describing the hydrogen coverage on the metal particles,

$$R \frac{d\theta}{d\tau} = 2P\alpha_p f_p - 2\beta_1 R\theta^2 - \lambda\theta\phi - \theta(1-\phi) - \eta\theta \quad (1)$$

$$\frac{d\phi}{d\tau} = 2P\frac{\alpha_b}{R}(1-\phi)^2 - 2\frac{\beta_2}{R}\phi^2 - \lambda\theta\phi + \theta(1-\phi) \quad (2)$$

where the fractional coverage of weak and strong binding sites is represented by θ and ϕ , respectively. The ratio of total weak to strong binding sites is given by R , and f_p is the fraction of edge and corner sites that act as portals (those which are occupied by Ru atoms rather than Ag atoms). Dimensionless rate constants for the various mechanisms of adsorption, desorption, and spillover have been derived by normalizing them with the rate constant for the movement of weakly bound hydrogen to strong binding sites. The resulting dimensionless parameters and variables are defined in Table 1 and in Notation.

The spillover rate has been assumed to be first order in the fractional coverage of weak binding sites on the metal particles; spillover from strong binding sites is not allowed. Once on the support, atomic hydrogen can diffuse and desorb associatively. Therefore, the fractional coverage of hydrogen on the amorphous silica support, ψ , can be represented by the following dimensionless equation and associated boundary conditions:

$$\frac{\partial \psi}{\partial \tau} = \frac{\alpha}{\chi} \frac{\partial}{\partial \chi} \left(\chi \frac{\partial \psi}{\partial \chi} \right) - \psi^2 \quad (3)$$

$$-\frac{\partial \psi}{\partial \chi} \Big|_{\chi=1} = \frac{k_{sp} W_0}{2\pi \rho D} \theta \quad (4)$$

$$\frac{\partial \psi}{\partial \chi} \Big|_{\chi=\chi_{mid}} = 0 \quad (5)$$

The radial distance from the center of a circular metal particle to a location on the support is represented in the polar coordinate, χ , with units of the radius of a typical Ru particle, as shown in Figure 1. The parameter, α , is the ratio of the surface diffusion coefficient on the support to the desorption rate constant. The spillover flux from the metal particle to the support is defined by equation (4); the minimum hydrogen concentration occurs at a radial coordinate halfway between nearest neighbor metal particles, as described by equation (5).

Irreversibility is an important characteristic of the portal model described by eqs. (1) - (5). In particular, hydrogen is assumed to adsorb irreversibly through portals onto weak binding sites where it can either spill over (irreversibly) or move to strong binding sites (also irreversibly). Desorption then occurs either on the metal particle basal planes or on the support. Although this lack of microscopic detailed balance makes the model unsuitable for describing thermodynamically closed systems, adsorption studies are carried out under isothermal conditions far from equilibrium.

Experiment

Sample Preparation

All catalysts used in the present work were prepared by the incipient wetness impregnation technique. Ruthenium nitrosyl nitrate solution (Strem Chemical, 1.5 wt % Ru) and silver nitrate salt (Johnson-Matthey) were used as precursors for Ru and Ag, respectively. Fumed silica (Cab-O-Sil HS5, BET surface area 300 m²/g) was used as support. An appropriate amount of the aqueous solution of the Ru precursor was added to the silica support so that the loading of Ru was 4 wt % of total content of Ru and SiO₂. This slurry was dried overnight at room temperature and for two hours at 383 K in a furnace. The dried sample was subsequently reduced in flowing hydrogen at 673 K and atmospheric pressure for 4 hours. Ru-Ag/SiO₂ samples were prepared by sequential impregnation of the reduced sample by adding the required amount of AgNO₃ salt in water so that the solution was 2.2 ml per gram of the support. The Ag concentration was between 1 and 30 atomic percent of the atoms of the metal. The resulting slurry was dried and reduced in hydrogen as described before. The samples were then washed 6 to 8 times with 60 ml of hot nanopure water (18 MΩ cm⁻¹) to remove any chlorine impurities. Finally, washed samples were dried and reduced before use in dispersion studies and chemisorption experiments.

Dispersion Measurement

Dispersion of 4 wt % Ru/SiO₂ and Ru-Ag/SiO₂ was measured by selective hydrogen chemisorption in a glass apparatus described elsewhere (Wu *et al.*, 1989). The dispersion measurements were made by following the optimized volumetric technique of Uner *et al.* (1995). About 1 g of the sample was placed in a Pyrex sample cell and heated at 400 K for 30 minutes in the presence of helium and evacuated for removal of moisture. Thereafter, the sample underwent static reduction in hydrogen at 673 K and 1 atm. The hydrogen was replenished every 30 minutes, and the reduction was carried out for 4 hrs. After reduction, the sample was evacuated at 400 K for 4 hrs and then cooled to room temperature. The total hydrogen uptake of the catalyst was measured by exposing the sample for 10 minutes each to successive hydrogen pressures of 10, 20, 30, and 40 Torr at 335 K. The sample was then evacuated to less than 10⁻⁵ Torr for 10 minutes to remove the weakly bound hydrogen. The uptake of weak hydrogen was then measured by repeating the procedure described above. The total amount of strongly adsorbed, weakly adsorbed, and spillover hydrogen can be obtained by extrapolating the low pressure linear portions of the total hydrogen uptake curves to zero pressure. Extrapolation of the low pressure linear portion of the weakly bound hydrogen isotherm to zero pressure gives a good estimate of the amount of weakly bound and spillover hydrogen. Note that because of short exposure times, the amount of spillover

hydrogen is expected to be small. The amount of strongly bound hydrogen can be found from the difference of the above two values. The metal dispersion can then be determined from the amount of strongly bound hydrogen by assuming one-to-one stoichiometry between the hydrogen and surface Ru metal atoms of the Ru particle.

The measured dispersions of four catalyst samples with loadings of 4 wt % Ru/SiO₂ and with different amounts of silver are listed in Table 2. In each case, the dispersion was determined to be approximately 20 %. If the metal particles are assumed to have a cubooctohedral structure, then approximately 15 % of the surface atoms reside at portal sites. In principle, if silver atoms always populate portal sites before basal plane sites, as little as 3 at % Ag is required to block all portals.

H₂ Adsorption Measurements

Hydrogen adsorption measurements were carried out on samples reduced with hydrogen and evacuated at 673 K for 4 hrs. The samples were then exposed to hydrogen (Research Grade, Voltaix) at 400 K and pressure readings were taken after 30 minutes. Hydrogen pressure was progressively increased from less than 1 Torr to 800 Torr. For each sample studied, a total of 14 data points were taken at various pressures.

Comparison of Model with Experiments

Parameter Estimation

For high concentrations of silver, all portal sites should be blocked ($f_p = 0$, rendering weak binding sites inaccessible) and the portal model defined by Eqs. (1)-(5) reduces to the conventional Langmuir model:

$$\frac{d\phi}{d\tau} = 2P \frac{\alpha_b}{R} (1 - \phi)^2 - 2 \frac{\beta_2}{R} \phi^2 \quad (6)$$

Hence, the dimensionless rate constants for adsorption and desorption on basal planes, α_b and β_2 , were estimated from a least squares fit of Eq. (6) to submonolayer isotherm data for catalyst samples containing 30 at % Ag, as shown in Figure 2. In fitting Eq. 6 to this data, the ratio of the number of weak and strong binding sites, R , has been assumed to be unity. The dimensionless spillover rate constant, η , has been deduced from experimental data obtained by Uner *et al.* (1995). The remaining non-adjustable portal model parameters, α_p , β_1 and λ , were estimated from a least squares fit of Eqs. (1) and (2) to isotherm data obtained for a pure ruthenium sample ($f_p = 1$), as shown in Figure 2. The fraction of unblocked portal sites, f_p , which depends upon the silver content of a given catalyst, was used as an adjustable parameter in the comparison of portal model predictions with experiments using bimetallic catalysts.

The values of the dimensionless adsorption and desorption rate constants for strongly bound hydrogen listed in Table 1 are consistent with rate constants obtained from selective excitation NMR by Savargaonkar *et al.* (1998). The dimensionless rate constants for strong-strong, strong-weak, and weak-weak hydrogen desorption are also in the expected increasing order. Lastly, we note that the rate constant for hydrogen adsorption through portal sites is much larger than the rate constant for adsorption from the gas directly to strong binding sites.

Effect of Ag concentration

Portal model predictions and experimental adsorption isotherms on Ru-Ag/SiO₂ bimetallic catalysts containing intermediate amounts of Ag are also shown in Figure 2. As expected, the amount of hydrogen adsorbed per surface ruthenium atom decreases at all pressures as the silver concentration in the catalyst increases. For the catalyst samples with 4 and 10 at % Ag, the fraction of unblocked portal sites (f_p) were determined to be 0.4 and 0.1, respectively.

Figure 3 shows the portal model prediction of the distribution of adsorbed hydrogen between the three possible states: strongly adsorbed, weakly adsorbed, and spillover hydrogen. The strong binding sites are filled at very low hydrogen pressure, whereas weak binding sites are populated at higher pressures. Notice that spillover hydrogen represents a significant

fraction of the total hydrogen adsorbed. Addition of Ag into the metal particle decreases the amount of both weakly bound and spillover hydrogen. For example, most of the adsorbed hydrogen on Ru-Ag/SiO₂ containing 30 at % Ag exists in a strongly bound state.

Figure 4 shows the amount of spillover hydrogen on the silica support as a function of the coverage of weakly bound hydrogen on Ru metal particles. It can be observed that even at a very low coverage of weakly bound hydrogen on the metal particles, a significant amount of spillover hydrogen resides on the support.

Fraction of surface atoms which lie on the edges and corners of the metal particle increases as the dispersion of the metal is increased. This relationship is presented in Figure 5. The remaining fraction of the surface atoms constitute the basal plane atoms. Figure 6 shows the hydrogen adsorption isotherm as the fraction of portal sites containing ruthenium is increased.

Discussion and Conclusions

A significant fraction of surface atoms on highly dispersed supported metal particles reside at low coordination edge and corner sites, and these sites can be considered to possess properties similar to those at the stepped surfaces of a single crystal. Because of the immiscibility of ruthenium and

silver, silver preferentially populates these edge and corner “portal sites”, effectively blocking hydrogen access to weak binding states. This in turn leads to a decrease in the amount of spillover hydrogen.

A fit of the portal model to experimental isotherm data shows that the adsorption rate constant is higher for portal sites than for basal plane sites. Furthermore, the desorption rate constant for weak-weak association was found to be much greater than for weak-strong association, which in turn is higher than for strong-strong hydrogen desorption. These results are reasonable since the activation energy for associative desorption of two strongly bound hydrogen atoms (estimated from the initial heat of adsorption (Narayan, 1997) is approximately 90 kJ/mole. A transition-state theory estimate of the preexponential factor for associative desorption of mobile adsorbed species is 10^8 s^{-1} ; for immobile species it is 10^{13} s^{-1} (Dumesic *et al.*, 1993). Hence, from the ratio of the rate constants for strong-strong and weak-weak desorption, the activation barrier for weak-weak desorption can be estimated to be 20 kJ/mole.

The kinetics of spillover processes are slow compared to hydrogen adsorption on Ru metal. From the spillover model, the apparent diffusion coefficient of atomic hydrogen on the silica support is estimated to be $10^{-16} \text{ cm}^2/\text{s}$ at 400 K. Such a low value of diffusivity is probably due to the amorphous nature of the support and is consistent with estimates in the

literature (Robell *et al.*, 1964; Fleisch and Abermann, 1977). The rate constant for the associative desorption of hydrogen on SiO₂ was found to be 0.07 s⁻¹.

The portal model of hydrogen adsorption is able to explain the reduction in the amount of hydrogen adsorbed per surface ruthenium atom, on addition of Ag to Ru/SiO₂ catalysts. Addition of Ag to Ru/SiO₂ simulates the effect of increasing the Ru particle size by selectively populating edge and corner sites.

Acknowledgments

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Notation

D	Diffusivity of spillover H on the surface of the silica support
N	Total number of surface atoms on the metal particles
N_b	Number of adsorption sites on the basal planes
N_{pT}	Total number of portal sites on the surface of a Ru particle
S	Number of strong binding sites occupied
S_0	Total number of strong binding sites
W	Number of weak binding sites occupied

W_0	Total number of weak binding sites
c	number of spillover hydrogen atoms per unit area of the support ($= \rho\psi$)
f_p	fraction of portal sites with ruthenium atom
k_{abs}	adsorption rate constant for strong binding hydrogen on basal planes
k_{ap}	adsorption rate constant for adsorption through portals
k_{d2}	desorption rate constant for desorption from combination of one weakly and one strongly bound hydrogen
k_{db}	desorption rate constant for desorption of weakly bound hydrogen
k_{dbs}	desorption rate constant of strong binding hydrogen
k_m	rate constant of interaction between a weakly bound hydrogen atom and an empty strong binding site leading to a strongly bound hydrogen atom on basal planes
k_{sp}	rate constant of spillover of weakly bound hydrogen atoms from metal particle to the support
P	pressure
R_p	radius of the metal particle
r	distance from the center of a metal particle to a location on the support which is under the influence of that metal particle for spillover
ψ	coverage of spillover hydrogen on the support
ξ	Fraction of surface atoms as portals
ρ	spillover hydrogen adsorption site density on the support
$\theta = \frac{W}{W_0}$	

$$\phi = \frac{S}{S_o}$$

$$\tau = k_m W_o t$$

$$\chi = \frac{r}{R_p}$$

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Table Captions

Table 1: Model parameters. All parameters are dimensionless except α_p and α_b .

Table 2: Dispersion of the Samples

Table 1

$\alpha_p = \frac{k_{ap} N_{PT}}{k_m S_o W_o}$	1.0×10^{-6}
$\alpha_b = \frac{k_{abs}}{k_m}$	1.0×10^{-7}
$\beta_1 = \frac{k_{db}}{k_m}$	3.0×10^{-2}
$\beta_2 = \frac{k_{abs}}{k_m}$	1.4×10^{-5}
$\lambda = \frac{k_{d2}}{k_m}$	1.0×10^{-4}
$\eta = \frac{k_{sp}}{k_m S_o}$	1.0×10^{-8}
R	1
f_p	adjustable

Table 2

Sample	Atomic % Ag	Ru Dispersion (%)
Ru/SiO ₂	0	20.4
Ru-4 at % Ag/SiO ₂	4	19.8
Ru-10 at % Ag/SiO ₂	10	19.0
Ru-30 at % Ag/SiO ₂	30	16.2

Figure Captions

- Figure 1: Schematic of a metal particle (Figure 1a.) and the region of support under its influence for hydrogen spillover (Figure 1b.).
- Figure 2: Hydrogen Adsorption Isotherm on Ru-Ag/SiO₂ at 400 K obtained from the experiment and portal model of hydrogen adsorption. The concentration of Ag is 0, 4, 10, and 30 at % of total metal atoms. The value of the fraction of the available portal sites, f_p , is also mentioned.
- Figure 3: Distribution of states of hydrogen on Ru/SiO₂.
- Figure 4: Amount of spillover hydrogen on the silica support as a function of the coverage of weakly bound hydrogen on Ru metal particles.
- Figure 5: Fraction of total surface Ru atoms occupying the portal and basal sites on the metal particle as a function of dispersion of the catalyst.
- Figure 6: Hydrogen Adsorption Isotherm on Ru-Ag/SiO₂ at 400 K obtained from the model. The arrow indicates the increasing fraction of portal sites. For Ru/SiO₂ the fraction of portal sites available is 1.

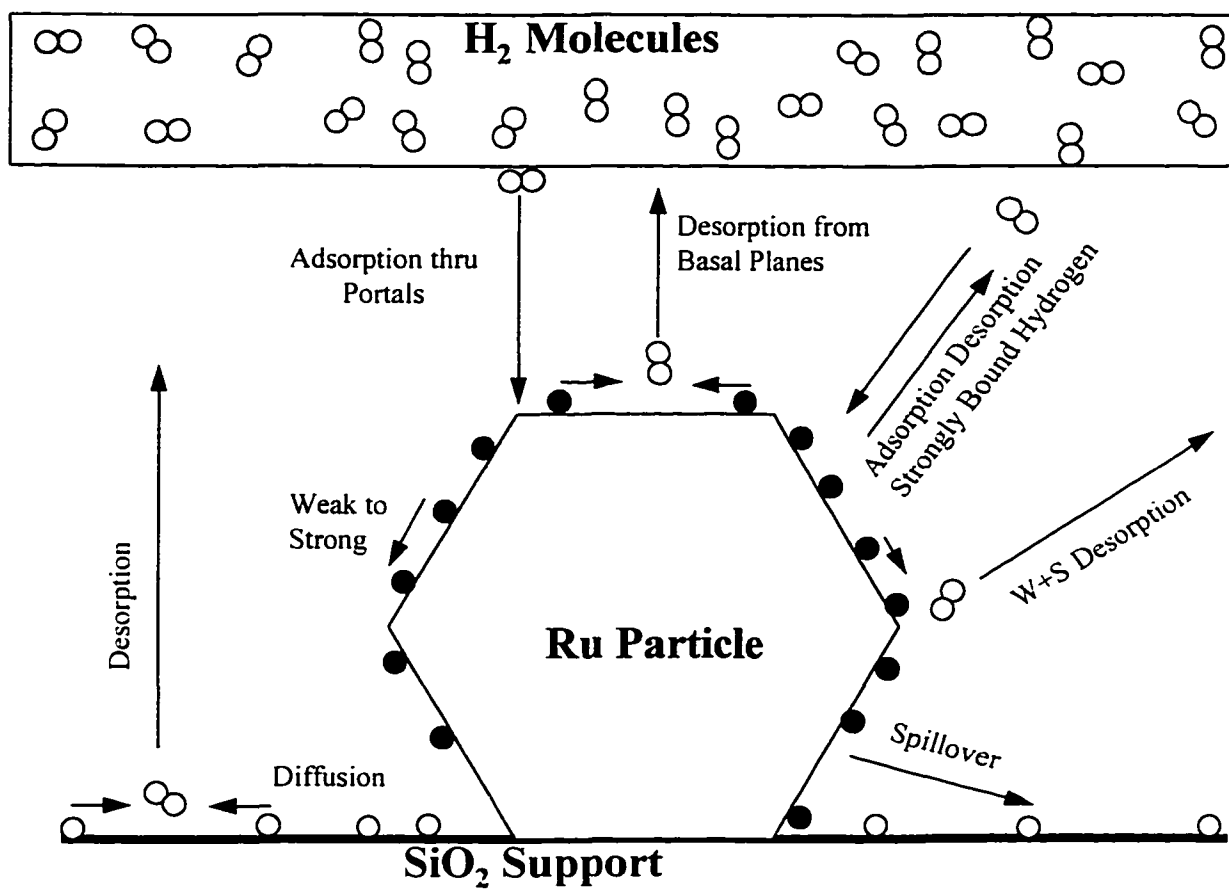


Figure 1(a).

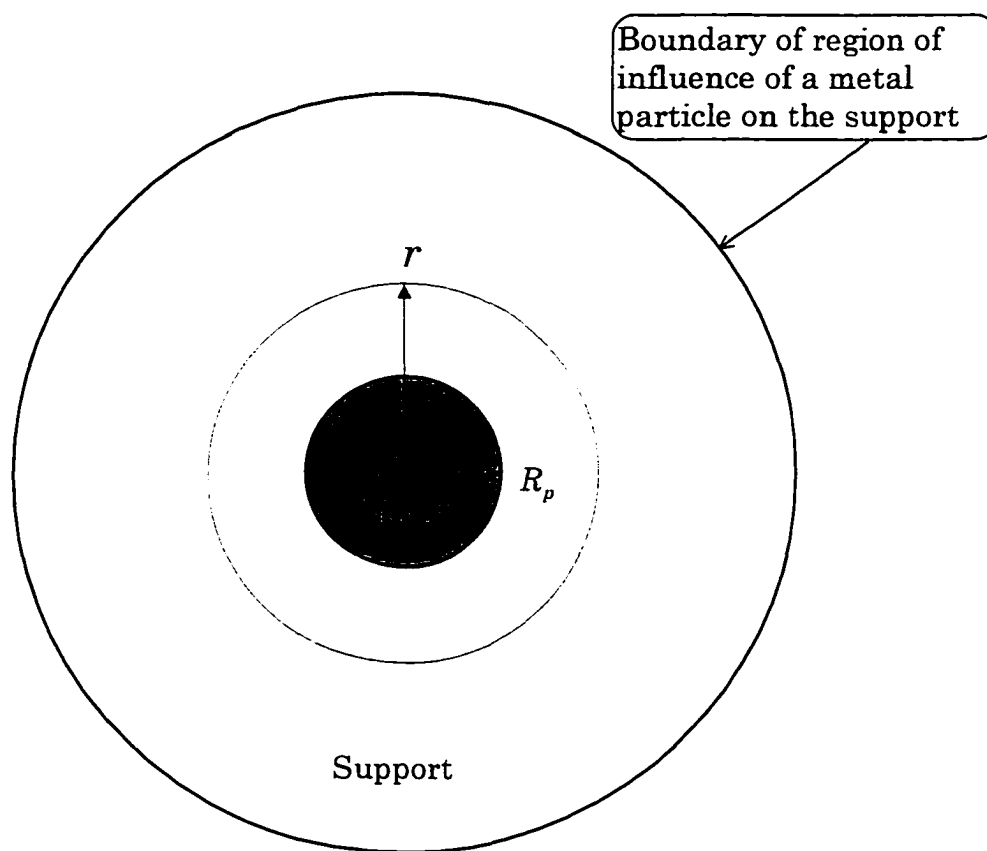


Figure 1(b).

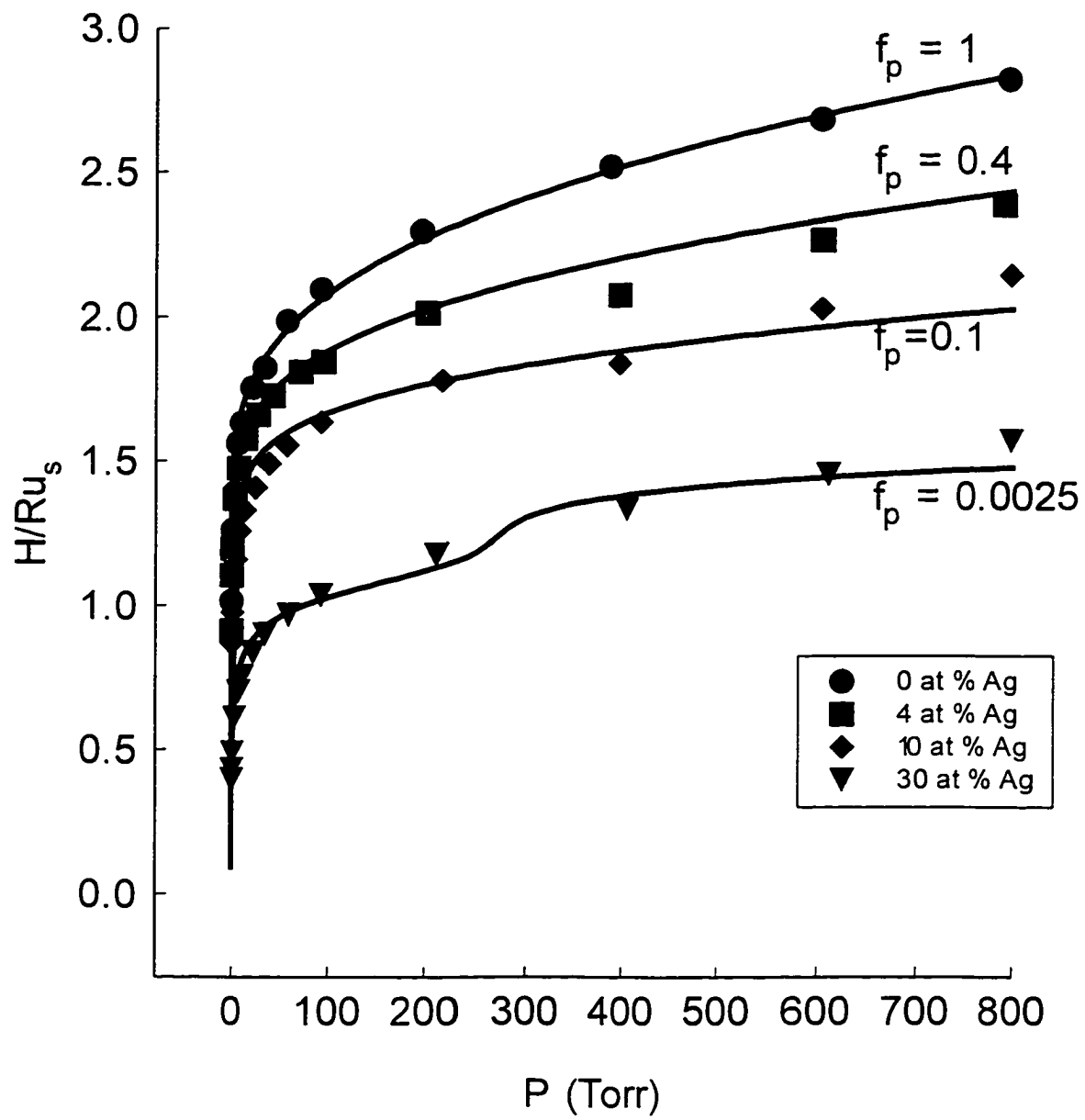


Figure 2.

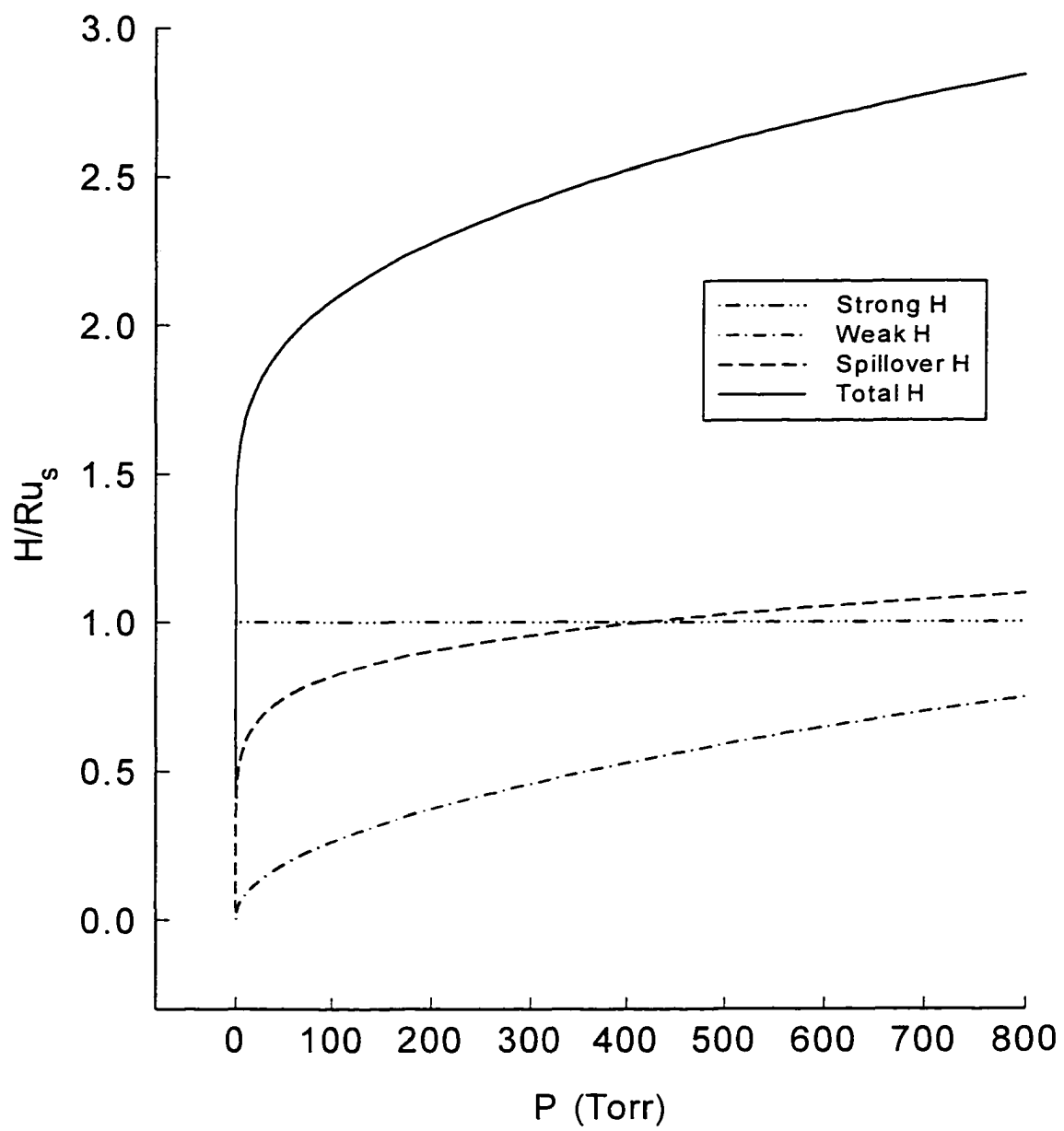


Figure 3.

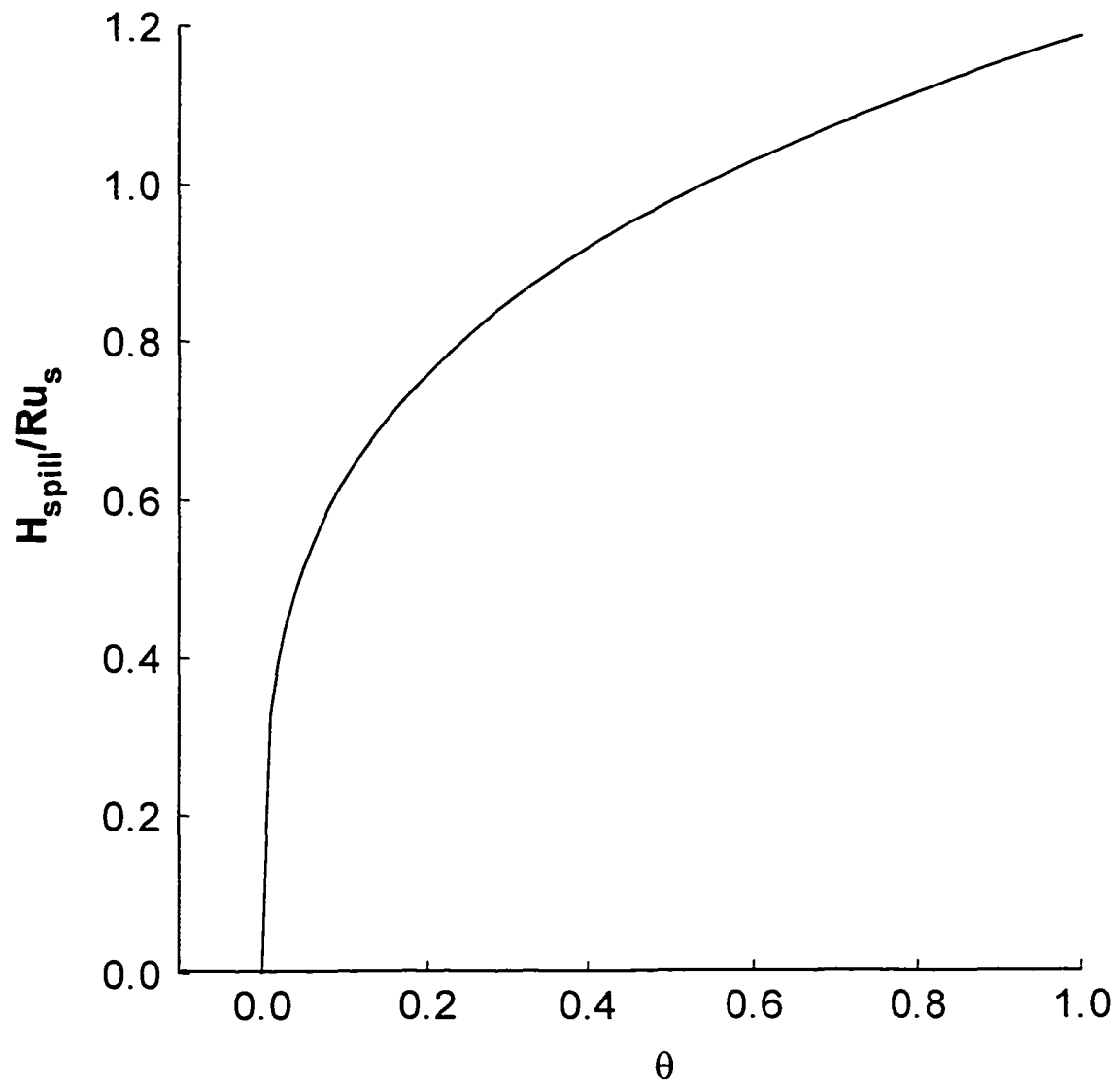


Figure 4.

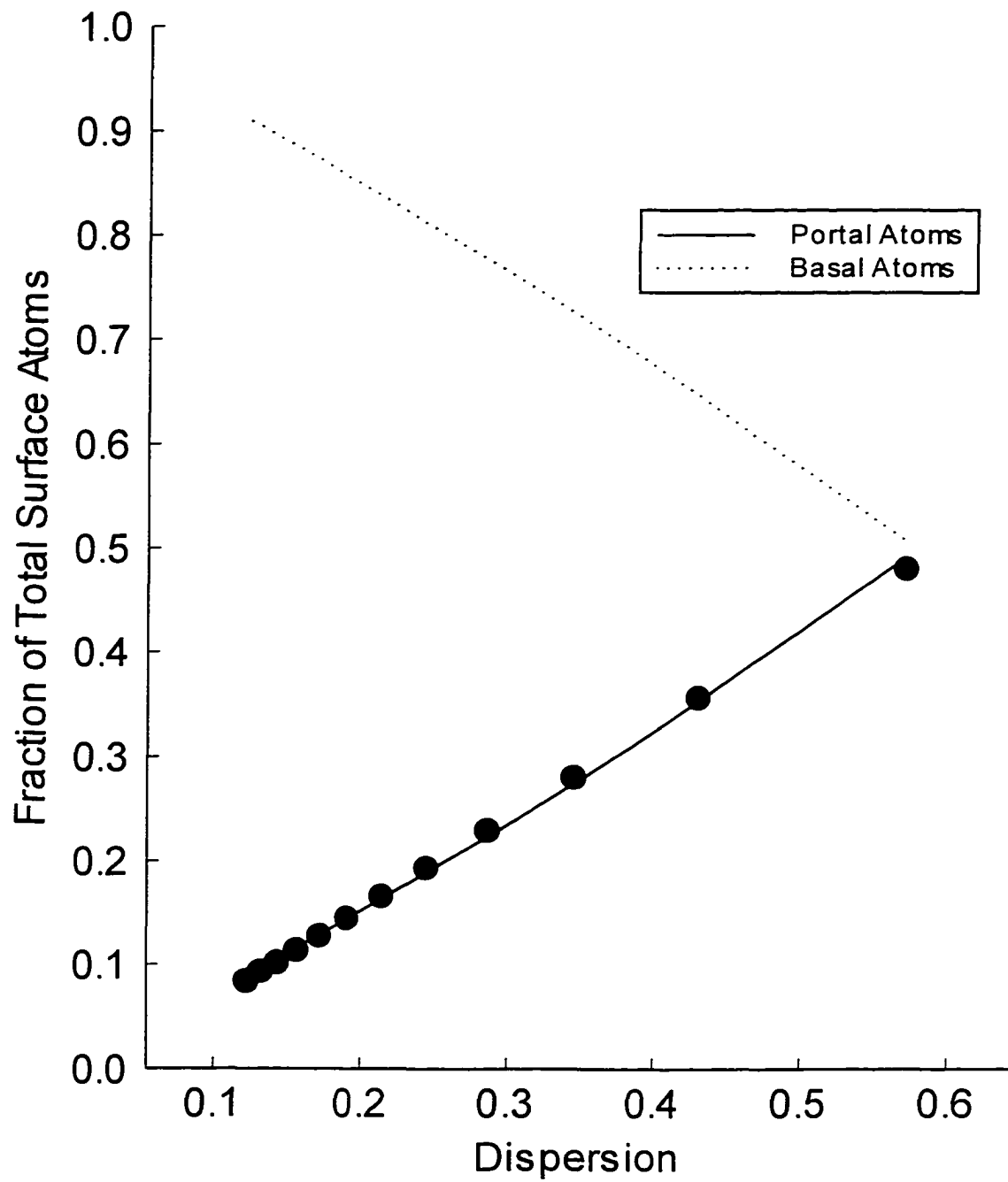


Figure 5.

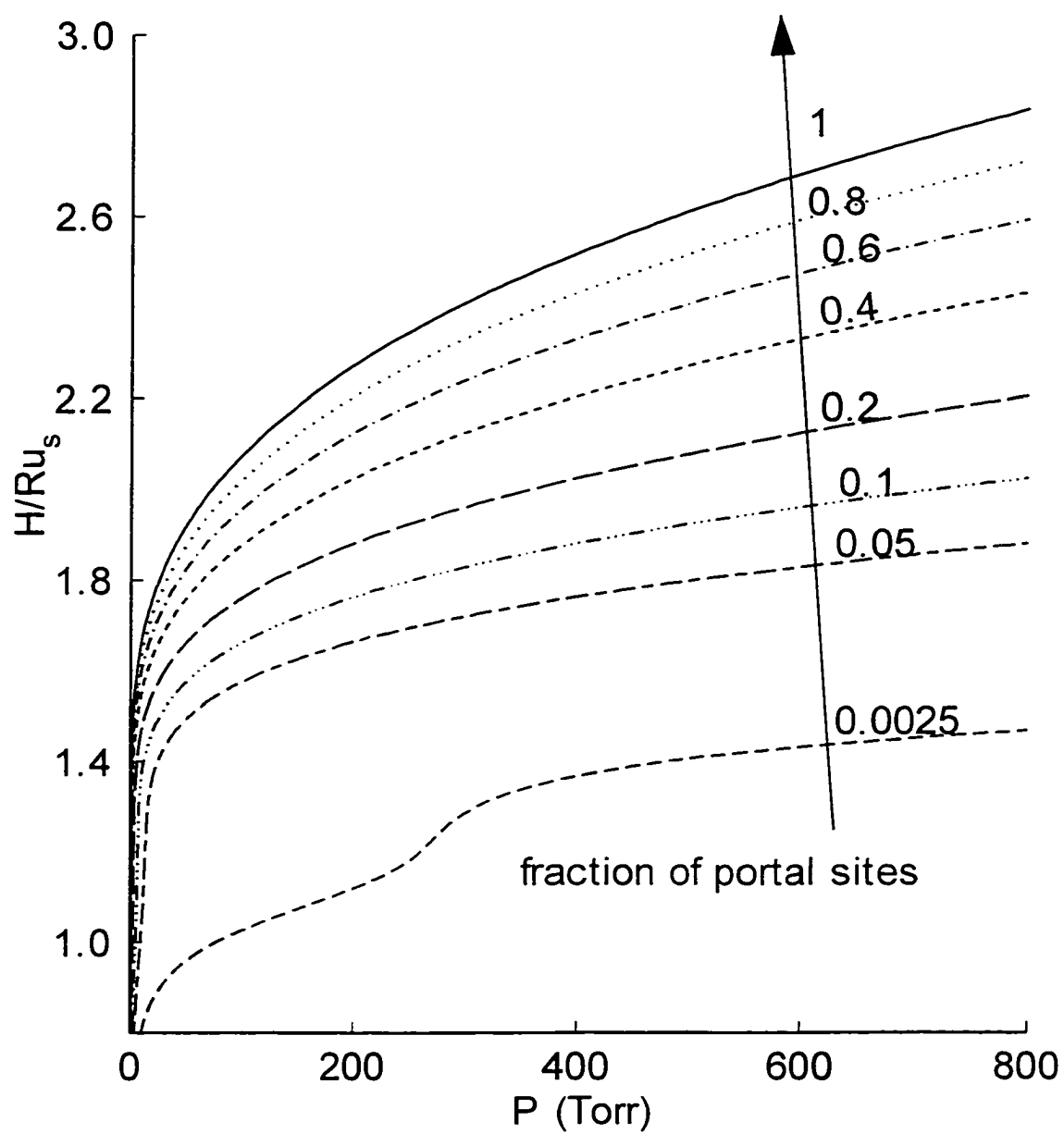


Figure 6.

CHAPTER 4. INVESTIGATING KINETICS OF ETHANE HYDROGENOLYSIS ON Ru AND Ru-Ag/SiO₂ CATALYSTS USING THE PORTAL MODEL OF HYDROGEN ADSORPTION

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Abstract

The *portal* model of hydrogen adsorption on Ru and Ru-Ag systems supported on silica was applied to study the kinetics of ethane hydrogenolysis.

Experimental data have shown that the apparent order of hydrogenolysis reaction with respect to hydrogen changes from -1.4 to -2.4 when Ag is added to Ru/SiO₂. The model was able to explain the above change in the apparent order of reaction with respect to hydrogen. A reaction mechanism was proposed which included the dual site-energy multiplicity of the *portal* model of hydrogen adsorption. At steady state the coverage of weakly bound hydrogen on Ru was drastically reduced when 40 at % Ag was added to it. The depletion of weakly bound hydrogen increased the extent of dehydrogenation of the [C₂H₅*] species which led to a more negative order of reaction with respect to hydrogen.

Keywords: Ethane Hydrogenolysis, Portal Model, Hydrogen Adsorption, Negative Order of Reaction, Dehydrogenation, Ru, Ag, SiO₂.

Introduction

Hydrogenolysis of a hydrocarbon involves the rupture of a carbon-carbon bond which is accompanied by hydrogenation to form two molecules from one. Hydrogenolysis of paraffins is of great importance in petroleum and petrochemical industries, in which it is sometimes a desired reaction as in hydrocracking, and sometimes not as in catalytic reforming of naphtha. Catalytic hydrogenolysis of ethane is generally used as a model reaction as ethane is the simplest molecule with a C-C bond whose cleavage leads to formation of only one product, methane. Kinetics of this reaction has been investigated by various researchers. Sinfelt [1-3] has reported the kinetic parameters for ethane hydrogenolysis on Group VIII transition metals supported on silica. The apparent order of reaction with respect to ethane was in the range of 0.6-1.0 for the various metals. However, with respect to hydrogen the apparent order of hydrogenolysis was found to be negative, between -0.8 and -2.5, except for Fe. In the case of Fe, the order of reaction was positive, 0.5. Catalytic reactions involving hydrogen and hydrocarbons as in hydrogenolysis, isomerization and deuterium exchange, frequently, show a negative-pressure dependency on the partial pressure of hydrogen.

Smale and King [4] have investigated the kinetics of ethane hydrogenolysis over bimetallic catalyst, Ru-Ag, supported on silica. The apparent order of reaction with respect to hydrogen was about -1.4 for pure ruthenium catalyst. In the case of bimetallic catalyst, Ru-40 at % Ag/SiO₂, the apparent order of reaction with respect to hydrogen was found to be -2.4. With respect to ethane the apparent order of reaction was found to be 0.8 for both Ru as well as Ru-Ag bimetallic catalysts. The above change in the order of the reaction on addition of Ag to Ru/SiO₂ was explained on the basis of a decrease in the rate constant (from very large to very small) for desorption of hydrogen from the surface of ruthenium particles.

Supported metal catalysts typically consist of particles with sizes less than 10 nm. Because of the small crystallite size, low coordination number sites such as edges and corners represent a significant fraction of all surface sites. These sites play an important role in interaction of the adsorbing gases on the metal surface. A *portal* model of hydrogen adsorption on Ru and Ru-Ag catalysts supported on silica has been developed by the author [5] which takes into account the changes in kinetics of hydrogen adsorption on addition of Ag to Ru/SiO₂.

Addition of Ag to Ru particles is known to change the hydrogen adsorption kinetics. Silver can also be expected to change the kinetics of hydrocarbon intermediates in the elementary reaction steps of the

hydrogenolysis reaction through its effect on hydrogen adsorption. The objective of the present research is to explain the change in the apparent order of hydrogenolysis reaction with respect to hydrogen for Ru and Ru-Ag catalysts using the portal model of hydrogen adsorption.

Reaction Mechanisms of Ethane Hydrogenolysis

The overall reaction of ethane hydrogenolysis is:



The above equation can be expressed in the general form of power rate law:

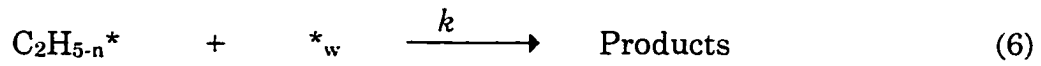
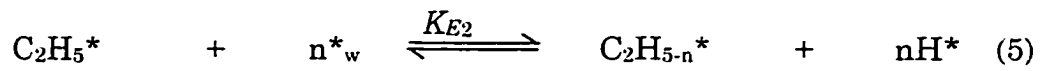
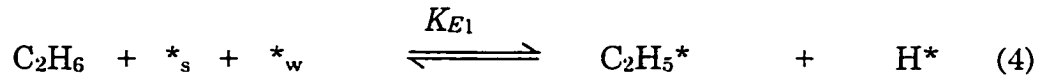
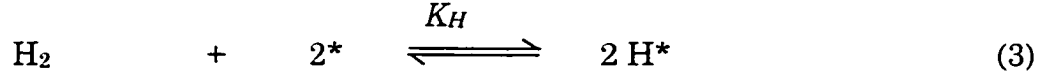
$$\text{rate} = k_1 [P_E]^\alpha [P_H]^\beta \quad (2)$$

In Eqn. (2), α and β are the apparent order of reaction with respect to ethane and hydrogen, respectively and P_E and P_H represent the respective partial pressure of ethane and hydrogen in the gas phase.

The mechanism of ethane hydrogenolysis over Group VIII metals is generally believed to include the following steps [6]: (i) hydrogen is adsorbed on the surface of the catalyst in atomic form, (ii) ethane adsorbs dissociatively on the catalyst surface with the breaking of a C-H bond, (iii) the C_2H_5 species formed from (ii) undergoes further dehydrogenation to form C_2H_x species, (iv) the C-C bond of C_2H_x species is cleaved leading to formation of CH_y species, and (iv) CH_y species is hydrogenated to form methane which desorbs from the

surface of the catalyst. The step in which the C-C bond is broken is considered to be the rate determining step.

Ethane Hydrogenolysis Mechanism:



As in the *portal model* of hydrogen adsorption, the surface of the catalyst has two types of sites: strong binding and weak binding. Only the weakly bound hydrogen is assumed to be reactive in the hydrogenolysis reactions. The subscripts _s and _w represent the strong and weak binding sites, respectively. The ethane molecule is assumed to adsorb only on the strong binding sites. The first three reactions represented by Eqn. (3-5) are intended to be in a steady state rather than a true adsorption/desorption equilibria. Therefore, K_H , K_{E1} and K_{E2} can be considered *steady state* constants for Eqn. (3), (4) and (5), respectively. k is the rate constant of the limiting step in Eqn. (6) in which the carbon-carbon bond is cleaved.

$$\text{Rate} = k[\text{C}_2\text{H}_{5-n}^*][{}^*_w] \quad (7)$$

$$\text{Rate} = \frac{kK_{E1}K_{E2}P_E}{(K_H P_H)^{\frac{n+1}{2}} (1 + \sqrt{K_H P_H})} \quad (8)$$

The rate equation (8) will be used to explain the change in the apparent order of reaction with respect to hydrogen when Ag is added to Ru/SiO₂.

Results and Discussion

In the rate equation (8), hydrogen pressure is in denominator which would explain the negative order with respect to hydrogen. The two factors which can affect the order are n and K_H . The term, K_H , can be determined from the model developed for adsorption of hydrogen on Ru-Ag catalysts [5].

Previous work in our research group has determined that the apparent order of hydrogenolysis reaction with respect to hydrogen is -1.4 for Ru/SiO₂ and -2.4 for Ru-40 at % Ag/SiO₂ [4]. The kinetic studies were carried out in a temperature range of 500-550 K and the partial pressure of hydrogen was 585 Torr.

Let us first consider the case with Ru-Ag bimetallic catalyst. At a Ag concentration of 40 at % almost all the low coordination sites of Ru metal particles are expected to be occupied by Ag atoms. In the portal model of hydrogen adsorption this would correspond to $f_p \approx 0$. This condition leads to a very small concentration of weakly bound hydrogen on the surface of the Ru metal particles i.e. $[H^*]/[*_w] \approx 0$. As stated earlier, only the weakly bound form of hydrogen is believed to take part in the hydrogenolysis reaction. This would

mean that $K_H \ll 1$ and the order with respect to hydrogen is then simplified to

$-\frac{n+1}{2}$. The range of n can be estimated from the following reaction steps:



The above reaction steps, Eqn. (9-13), are the expanded form of Eqn. (5).

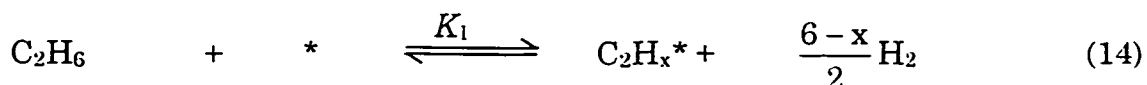
From the portal model when all the portals are closed or all the low coordination sites are occupied by Ag atoms the concentration of weakly bound hydrogen $[\text{H}^*]$ is negligible and $[*]$ is high. This condition would drive the above reactions to their right hand side which would lead to an increase in the amount of surface intermediates of the form C_2H_x with a low value of x . Put in another way, the value of n would be increased in C_2H_{5-n} . Theoretically, the maximum value of n can be 5 which means that all the hydrogen atoms are removed from the surface intermediate. However, it can be assumed that in the most likely scenario the surface intermediate is left with at least one hydrogen atom. This would mean that n is probably closer to 4 rather than 5. With $n=4$, the apparent order of the hydrogenolysis reaction is -2.5. This is in qualitative agreement with the experimentally observed value of -2.4 for the case in which Ru- 40 at % Ag/SiO₂ catalyst was used.

For Ru/SiO₂ catalyst, from the hydrogen adsorption model, the coverage of weakly bound hydrogen [H*] is 0.64 at 400 K and 585 Torr of hydrogen. Therefore, $\sqrt{P_H K_H} = \frac{[H^*]}{[*_w]} = 1.8$. The ethane hydrogenolysis reactions were carried out in a temperature range of 500-550 K which is much higher than the temperature in the adsorption model. A 100 K increase in the reaction temperature can significantly lower the term $\sqrt{K_H P_H}$. However, $\sqrt{K_H P_H}$ for Ru/SiO₂ will still be higher than its value in the case of Ru-Ag/SiO₂. This would mean there are less weak binding sites and more weakly bound sites are available for Eqn. (9-13) for Ru/SiO₂ than in Ru-Ag/SiO₂. Compared to the Ru-Ag system, this condition would drive the above reactions to their right hand side to a lesser extent in Ru/SiO₂. This would lead to an increase in the value of x in the surface intermediates of the form C₂H _{x} . A decrease in the extent of dehydrogenation of the surface intermediates means a decrease in the value of n in C₂H_{5-n}*. Therefore, the apparent order of hydrogenolysis with respect to hydrogen, $-\frac{n+1}{2}$, changes from -2.5 for Ru-Ag to -1.5 for Ag if correspondingly n changes from 4 to 2. In the case of Ru/SiO₂ both the factors of the denominator in Eqn. 8 are comparable to each other. The order of reaction with respect to hydrogen can be determined by combining the factors into a

single expression. This derivation is shown in Appendix F. The order of the reaction with respect to hydrogen is $-\frac{n+y}{2}$, where y lies between 1 and 2.

The negative order in hydrogen pressure is generally interpreted in terms of degree of dehydrogenation of the active intermediate on the surface of the catalyst [7]. The rupture of C-C bond occurs after the surface intermediate has undergone a series of dehydrogenation steps as shown in Eqn. (9-13). These reaction steps are inhibited by an increase in the partial pressure of hydrogen. Carbon-hydrogen bonds are activated readily when compared to carbon-carbon bond. The hydrocarbon is chemisorbed on the surface by breaking a carbon-hydrogen bond. The rate determining step involves the cleavage of C-C bond [1, 8, 9].

Cimino *et al.* [8] suggested the following mechanism for the hydrogenolysis of ethane on iron catalysts with or without alkali additions.



The species CH_y and CH_z are rapidly removed to the gas phase as methane.

The fractional coverage of surface with C_2H_x intermediate, θ , is approximated in a restricted range of pressure as:

$$\theta = \left(\frac{K_1 P_E}{P_H^{\frac{6-x}{2}}} \right)^n \quad (16)$$

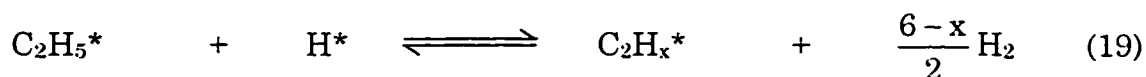
The rate of hydrogenolysis is given by the rate determining step of Eqn. (15):

$$r = k_2 \theta P_H = k_2' P_E^n P_H^{\left(1-n \frac{6-x}{2}\right)} \quad (17)$$

The variations in the apparent order of the reaction with respect to hydrogen for different catalysts were explained by assigning different values of x .

Assumed values of x were 0, 2 and 4 corresponding to acetylenic, acetylene and ethylene intermediates on the surface. They also suggested that highly dehydrogenating surfaces would lead to marked stripping of hydrogen from the hydrocarbon, which corresponds to low value of x in C_2H_x .

The mechanisms of hydrogenolysis reactions have been studied by Sinfelt *et al.* [3] by modifying Eqn. (14). For example, in one modification Eqn. (14) was divided into the following two steps:



The above modification along with an assumption that the rate of formation of C_2H_5 on the surface is just balanced by the rate of disappearance of C_2H_x via rupture of the C-C bond, the following rate expression was obtained:

$$r = \frac{b_1 P_E}{1 + b_2 P_H^{\left(\frac{6-x}{2}-1\right)}} \quad (20)$$

In the above equation, b_1 and b_2 are functions of the rate constants and effective equilibrium constants of the hydrogenolysis reactions.

In another modification the molecular hydrogen was left out from the rate determining step in Eqn. (15) which led to the following form of the rate equation for ethane hydrogenolysis [2]:

$$r = b_3 P_E^n P_H^{\left(-n \frac{6-x}{2}\right)} \quad (21)$$

In the above equation, b_3 is a function of the rate constants and effective equilibrium constants of the hydrogenolysis reactions.

Similar results regarding the extent of dehydrogenation of the adsorbed ethane species have been obtained by other researchers [10, 11]. For example, Gudkov *et al.* [11] have observed that in excess hydrogen on the catalyst surface the rate of hydrogenolysis is determined by the C-C bond rupture of ethane adsorbed in a mildly dissociative form of C_2H_5 . However, in excess hydrocarbon the rate is determined by the C-C bond rupture of ethane adsorbed in the deeply dissociated form of C_2H_2 .

Thus from the above results from the literature we observe that the rate of ethane hydrogenolysis reaction is affected not only by the kinetics of adsorptions of reactants hydrogen and ethane, but also by extent of dehydrogenation or dissociation of the forms of the adsorbed ethane intermediates. If there is less amount of hydrogen on the surface of the catalyst, the surface intermediate of the hydrocarbon can be in the form of C_2H_2 or C_2H species and if the surface has high amount of hydrogen the intermediate can be in the form of C_2H_3 or the less dehydrogenated

intermediates of the adsorbed C_2H_5 species. The above rate equations also show how the apparent order of reaction with respect to hydrogen can be dependent on the value of x in C_2H_x which takes part in the rate determining step of ethane hydrogenolysis.

In the case of Ru and Ru-Ag systems [4], addition of Ag to Ru/SiO₂ drastically reduces the stoichiometric ratio of adsorbed hydrogen to surface ruthenium. Ru/SiO₂ catalyst has much higher amount of surface hydrogen than Ru-40 at % Ag/SiO₂. The change in the hydrogen coverage on the surface of Ru particles also affect the extent of dehydrogenation or dissociation of the adsorbed hydrocarbon species, C_2H_5 . We believe that the change in the magnitude of x in C_2H_x leads to a change in the apparent order with respect to hydrogen. Thus on Ru/SiO₂ the apparent order of hydrogenolysis reaction with respect to hydrogen is -1.4 and in Ru-Ag/SiO₂ this order changes to -2.4.

Conclusion

By kinetic analysis and the application of *portal* model of hydrogen adsorption on Ru-Ag systems, it is shown that addition of Ag to pure Ru catalysts leads to a change in the apparent order of ethane hydrogenolysis reaction with respect to hydrogen. Addition of Ag leads to a decrease in the coverage of the reactive hydrogen on the surface of Ru metal particles. The change in the amount of hydrogen affects the degree of

dehydrogenation/dissociation of the adsorbed species of the hydrocarbon i.e. x in C_2H_x . This change can explain the change in order with respect to hydrogen from -1.4 for Ru/SiO₂ to -2.4 for Ru-Ag/SiO₂.

Acknowledgments

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CHAPTER 5. GENERAL CONCLUSIONS

The interaction of hydrogen with Ru and Ru-Ag catalysts supported on SiO_2 was investigated. A *portal* model based on the preferential adsorption of hydrogen through low coordination sites such as edges and corners of the Ru metal particles was developed using a rate equation approach. Hydrogen was adsorbed on the Ru metal either in a strongly bound form or in a weakly bound form. The weak binding hydrogen could spillover to the silica support. Even at low coverage of weak binding hydrogen on Ru metal, there was a significant amount of spillover hydrogen on the silica support. Hydrogen does not adsorb on Ag metal at the experimental conditions studied.

Our measurements of hydrogen adsorption onto supported Ru-Ag catalysts have shown marked decreases in the amount of hydrogen adsorbed relative to the amount adsorbed on Ru catalysts with no silver. This decrease in the stoichiometry of adsorbed hydrogen and surface Ru atoms could be explained by the portal model of adsorption of hydrogen. Addition of Ag to Ru/ SiO_2 led to the preferential occupation of edge and corner sites of Ru particle by silver atoms. Since hydrogen adsorption also occurs preferentially through these low coordination number sites, blocking of these sites by Ag atoms on which hydrogen does not adsorb leads to a decrease in the rate of hydrogen adsorption on the catalyst system. Addition of Ag does not directly affect the rate processes through which hydrogen desorbs. Thus on steady

state the total amount of hydrogen on the Ru-Ag is reduced due to a decrease in the hydrogen adsorption by closing of the portal sites and the continued desorption mechanisms. The decrease in the amount of adsorbed hydrogen occurs primarily by a decrease in the weakly bound hydrogen on the surface of the metal atoms. The low coverage of weak binding hydrogen also leads to a decrease in the amount of spillover hydrogen on the silica support.

The *portal* model of hydrogen adsorption was also applied to understand the kinetics of ethane hydrogenolysis on Ru-Ag/SiO₂ catalysts. The apparent order of hydrogenolysis reaction with respect to hydrogen has been determined to be about -1.4 for pure Ru catalyst supported on silica (Smale and King, 1990). In the case of bimetallic catalyst, Ru-40 at % Ag/SiO₂, the apparent order of reaction with respect to hydrogen was found to be -2.4. Addition of Ag leads to a decrease in the coverage of hydrogen on the surface of Ru metal particles. The change in the amount of hydrogen affects the degree of dehydrogenation/dissociation of the adsorbed species of the hydrocarbon i.e. n in C₂H_{5-n}. In the proposed reaction mechanism the apparent order of reaction with respect to hydrogen is related to n . A higher value of n leads to a more negative order of reaction. In the case of Ru-40 at % Ag/ SiO₂, all the portal sites are closed and the surface of the catalyst has negligible amount of weakly bound hydrogen. When ethane is adsorbed at these conditions the adsorbed species [C₂H₅*] can dehydrogenate to a greater extent i.e. n will be higher in

C_2H_{5-n} . This leads to an apparent order of reaction with hydrogen which is more negative compared to Ru/SiO₂ in which the coverage of weak binding sites with hydrogen is higher.

Therefore, the portal model of hydrogen adsorption is able to explain the decrease in the amount of adsorbed hydrogen on addition of Ag to Ru/SiO₂. The change in the apparent order of ethane hydrogenolysis with respect to one of its reactant, hydrogen, can also be reasonably explained with the help of the proposed mechanism of hydrogen adsorption on supported ruthenium catalysts.

Recommendations For Future Work

Ru-Ag bimetallic system was selected for the present work due to simple nature of interaction between Ru and Ag. Ru and Ag are immiscible in each other and Ag preferentially occupies the low coordination sites on the surface of the Ru particle. On the other end of the complexity spectrum are the industrially useful catalysts in which both the elements are from Group VIII such as Pt-Rh. Mixing of Pt and Rh on the surface of the metal particles is random. Surface composition of these particles under vacuum is different from its composition when the surface is exposed to hydrogen.

To understand the behavior of the complex bimetallic systems the next work should model the hydrogen adsorption for Ru-Cu system which is slightly more complex than Ru-Ag. Like Ag, Cu also segregates to the surface and preferentially populates the low coordination sites on the surface of the Ru

particles. However, unlike Ag, Cu can adsorb hydrogen directly from the gas phase, although the adsorption is an activated process. Also hydrogen adsorbed on Ru particles can move to copper atoms. Therefore, suitable terms for adsorption and desorption on and from copper have to be developed and added to the present model. Also the adsorption temperature needs to be varied in the experimental work so that adsorption through copper atoms can take place at higher temperature and be stopped at lower temperature.

APPENDIX A. DERIVATION OF PORTAL MODEL EQUATIONS FOR HYDROGEN ADSORPTION

Total number of surface atoms on the metal particles	=	N
Number of portal sites	=	N_p
Number of adsorption sites on the basal planes	=	N_b
Fraction of surface atoms as portals	=	ξ
Total number of weakly binding sites	=	W_o
Total number of strongly binding sites	=	S_o
Number of weakly binding sites occupied	=	W
Number of strongly binding sites occupied	=	S

Balance for Weakly Binding Sites

I. Rate of adsorption of hydrogen atoms through portals	=	$2 P k_{ap} N_p$
II. Rate of desorption through basal planes	=	$2 k_{db} W^2$
III. Desorption rate from combination of weak and strong	=	$k_{d2} W S$
IV. Movement rate from weak to strong	=	$k_m W (S_o - S)$
V. Spillover rate from metal particles to the support	=	$k_{sp} W$
Rate of Change of Weakly Binding Sites	=	$\frac{dW}{dt}$

$$\frac{dW}{dt} = I - II - III - IV - V$$

Balance for Strongly Binding Sites

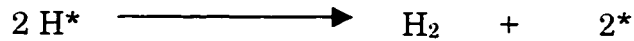
I. Rate of adsorption of hydrogen through basal planes	=	$2 P k_{abs} (S_o - S)^2$
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$$\begin{aligned}
\text{II. Rate of desorption from basal planes} &= 2 k_{dbs} S^2 \\
\text{III. Desorption rate from combination of weak and strong} &= k_{d2} W S \\
\text{IV. Movement rate from weak to strong} &= k_m W (S_o - S) \\
\text{Rate of Change of Strongly Binding Sites} &= \frac{dS}{dt}
\end{aligned}$$

$$\frac{dS}{dt} = I - \text{II} - \text{III} + \text{IV}$$

Modeling of Spillover on the Support

Hydrogen molecules dissociatively adsorb on the supported metal particles. Atomic hydrogen spills over from the metal particle to the support and then it diffuses and combines with another atom and then desorbs from the support. The desorption step can be written in the following manner:



Let us define the following terms:

$$\psi = \frac{\text{Number of Hydrogen Atoms on the Support}}{\text{Number of Sites on the Support}}$$

$$c = \frac{\text{Number of Hydrogen Atoms on the Support}}{\text{Area of the Support}}$$

$$\rho = \frac{\text{Number of Sites on the Support}}{\text{Area of the Support}}$$

$$c = \rho \psi$$

$$r_d = k \psi^2 = A \exp\left(\frac{-E_a}{RT}\right) \psi^2$$

$$r_d = \frac{\text{Change of Coverage}}{\text{Time}} = -\frac{d\psi}{dt}$$

$$\rho r_d = \frac{\text{Number of Hydrogen Atoms Desorbed}}{\text{Area of Support}}$$

Mass Balance of Hydrogen:

in - out - desorption = accumulation

$$-D \frac{\partial c}{\partial r} 2\pi r \Big|_r + D \frac{\partial c}{\partial r} 2\pi r \Big|_{r+\Delta r} - 2\pi r \Delta r \rho r_d = 2\pi r \Delta r \frac{\partial c}{\partial t}$$

$$\frac{\partial c}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) - \rho r_d$$

$$\frac{\partial \psi}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi}{\partial r} \right) - r_d$$

$$\frac{\partial \psi}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi}{\partial r} \right) - k \psi^2$$

$$\boxed{\frac{\partial \psi}{\partial \tau} = \frac{\alpha}{\chi} \frac{\partial}{\partial \chi} \left(\chi \frac{\partial \psi}{\partial \chi} \right) - \psi^2}$$

where:

$$\chi = \frac{r}{R} \quad \tau = k\tau \quad \alpha = \frac{D}{kR^2}$$

Boundary Conditions are:

$$-\frac{\partial \psi}{\partial \chi} \Big|_{\chi=1} = \frac{k_{sp} W_0}{2\pi \rho D} \theta$$

$$\frac{\partial \psi}{\partial \chi} \Big|_{\chi=\chi_{mul}} = 0$$

$$\frac{dW}{dt} = 2P k_{ap} N_p - 2k_{db} W^2 - k_{d^2} W S - k_m W (S_0 - S) - k_{sp} W \quad (1.1)$$

$$\frac{dS}{dt} = 2P k_{abs} (S_0 - S)^2 - 2k_{abs} S^2 - k_{d^2} W S + k_m W (S_0 - S)$$

$$\frac{dW}{dt} = 2P k_{ap} N_p - 2k_{db} W_0^2 \theta^2 - k_{d^2} W_0 S_0 \theta \phi - k_m W_0 S_0 \theta (1 - \phi) - k_{sp} W_0 \theta \quad (1.2)$$

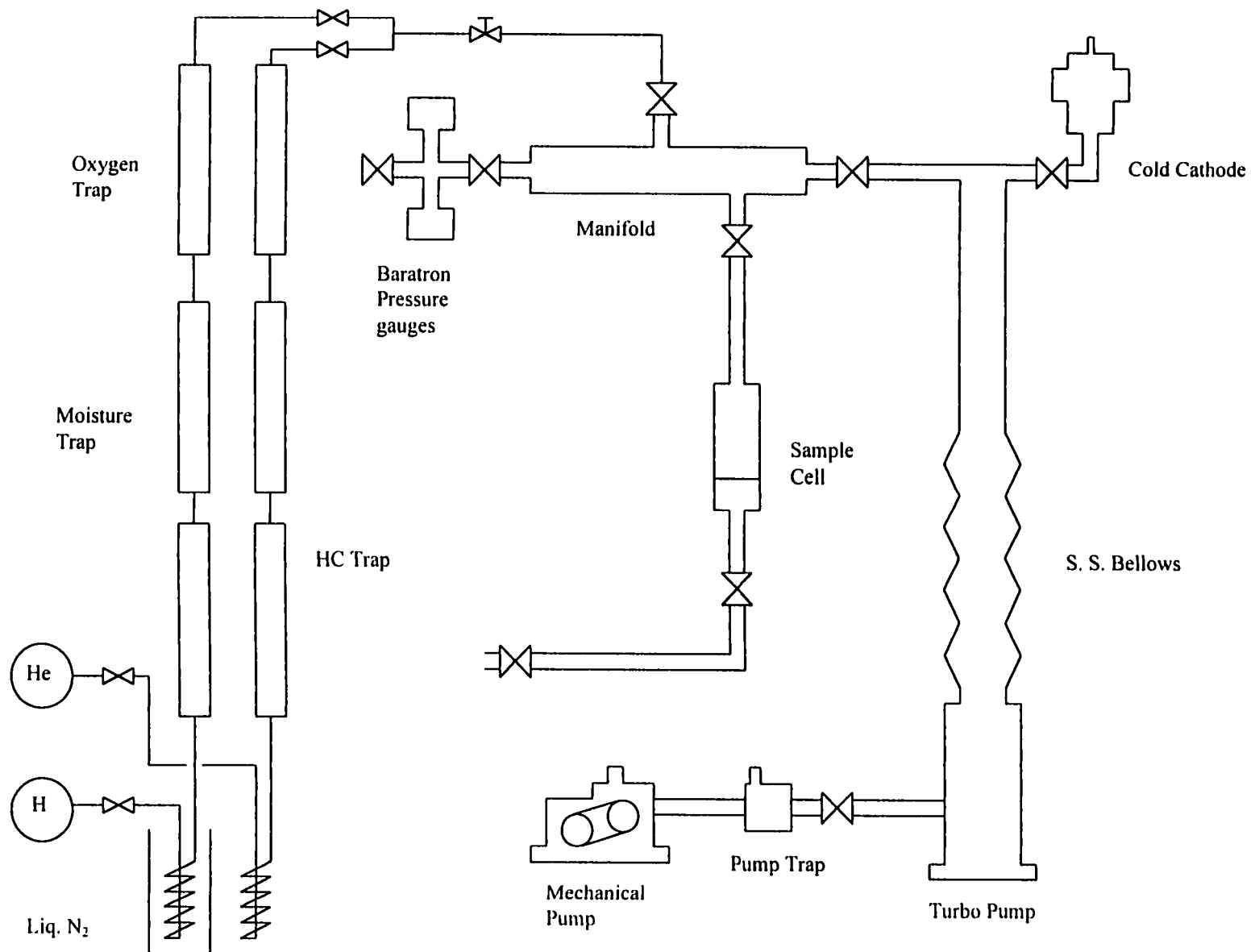
$$\frac{dS}{dt} = 2P k_{abs} S_0^2 (1 - \phi)^2 - 2k_{abs} S_0^2 \phi^2 - k_{d^2} W_0 S_0 \theta \phi + k_m W_0 S_0 \theta (1 - \phi)$$

$$\frac{1}{k_m S_0 W_0} \frac{dW}{dt} = 2P \frac{k_{ap}}{k_m S_0 W_0} N_p - 2 \frac{k_{db}}{k_m S_0} W_0 \theta^2 - \frac{k_{d^2}}{k_m} \theta \phi - \theta (1 - \phi) - \frac{k_{sp}}{k_m S_0} \theta \quad (1.3)$$

$$\frac{1}{k_m S_0 W_0} \frac{dS}{dt} = 2P \frac{k_{abs}}{k_m} \frac{S_0}{W_0} (1 - \phi)^2 - 2 \frac{k_{abs}}{k_m} \frac{S_0}{W_0} \phi^2 - \frac{k_{d^2}}{k_m} \theta \phi + \theta (1 - \phi)$$

$$\begin{aligned} R \frac{d\theta}{d\tau} &= 2P \alpha_r f_r - 2\beta_1 R \theta^2 - \lambda \theta \phi - \theta (1 - \phi) - \eta \theta \\ \frac{d\phi}{d\tau} &= 2P \frac{\alpha_b}{R} (1 - \phi)^2 - 2 \frac{\beta_2}{R} \phi^2 - \lambda \theta \phi + \theta (1 - \phi) \end{aligned}$$

APPENDIX B. SCHEMATIC OF THE EXPERIMENTAL SETUP



APPENDIX C. STRUCTURE SENSITIVE AND STRUCTURE INSENSITIVE REACTIONS

Structure Sensitive Reaction	Structure Insensitive Reaction
<i>Hydrogenolysis</i> Ethane on Ru Methylcyclopentane on Pt	<i>Ring Opening</i> Cyclopropane on Pt
<i>Isomerization</i> Isobutane on Pt Hexane on Pt	<i>Hydrogenation</i> Benzene on Pt Ethylene on Pt, Rh
<i>Cyclization</i> Hexane on Pt Heptane on Pt	<i>Dehydrogenation</i> Cyclohexane on Pt
<i>Hydrodesulfurization</i> Thiophene on Re	<i>Hydrodesulfurization</i> Thiophene on Mo
<i>Ammonia Synthesis</i> on Fe, Re	

APPENDIX D: ROLE OF ATOMIC STEPS

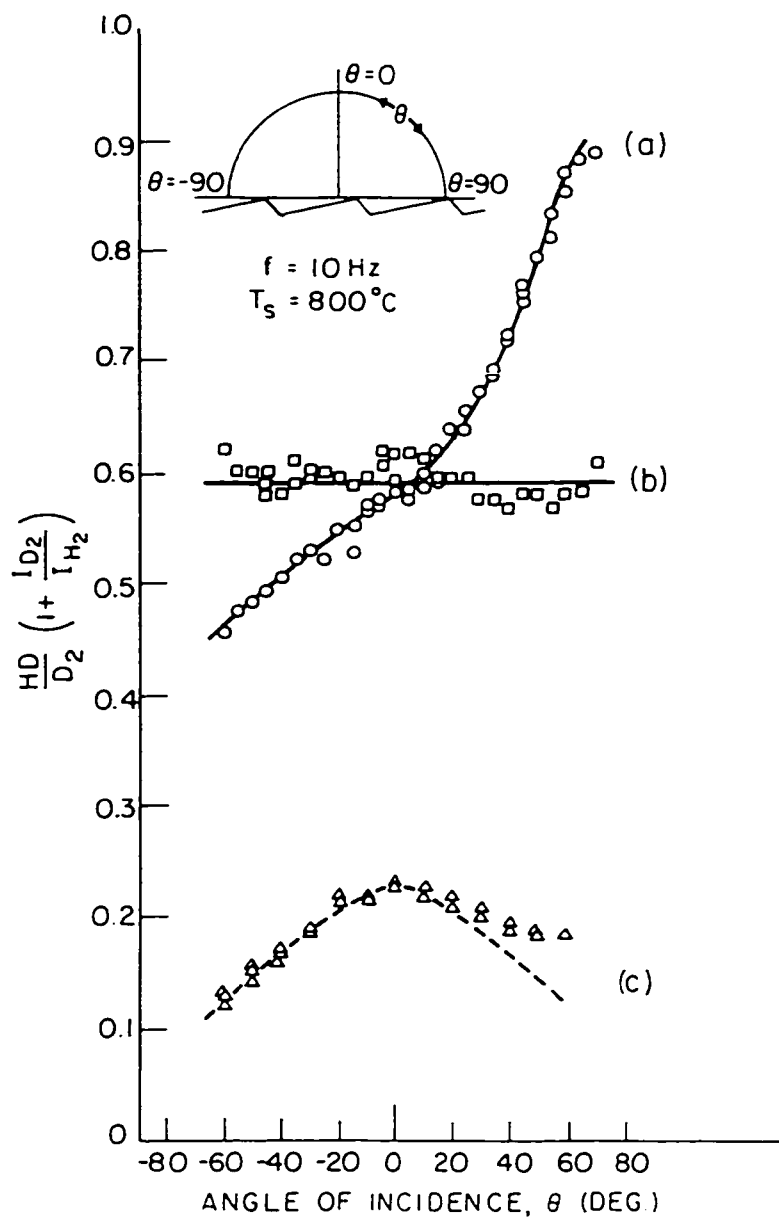


Figure D-1: Production of HD as a function of angle of incidence, θ , of the molecular beam, normalized to the incident D_2 intensity: (a) Pt(332) surface with the step edges perpendicular to the incident beam ($\phi = 90^\circ$); (b) Pt(332) where the projection of the beam on the surface is parallel to the step edges ($\phi = 9^\circ$); (c) Pt(111). (Zaera and Somorjai, 1988).

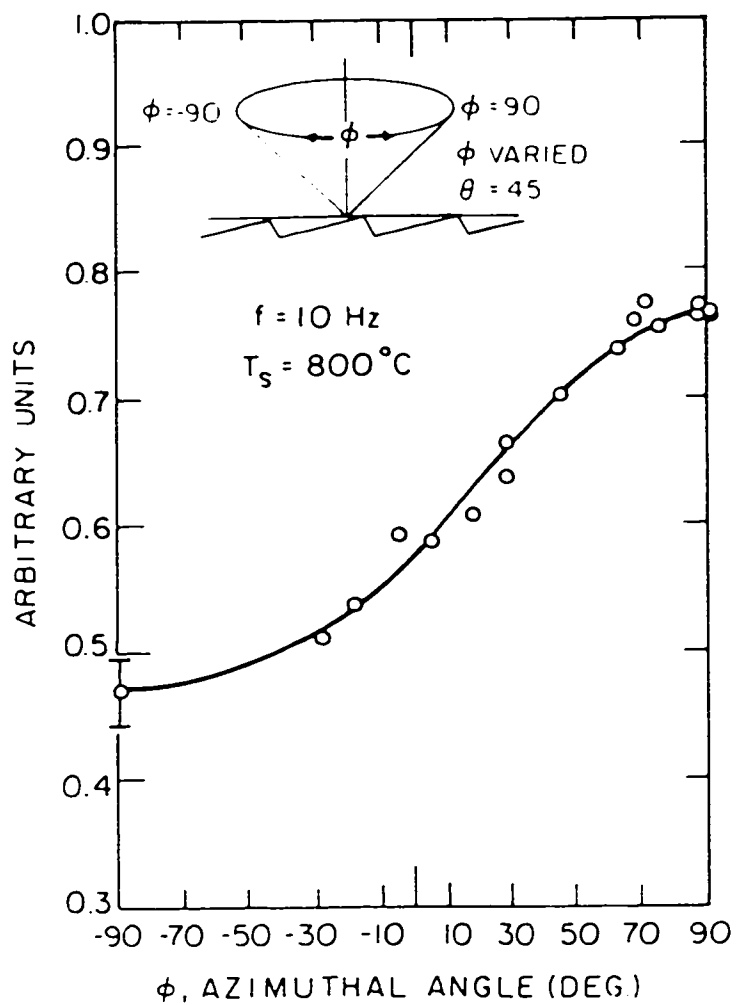


Figure D-2: Variation of HD production with azimuthal angle of the molecular beam on the Pt(s)-[6(111) \times (111)]. The angle of incidence is fixed at 45° , measured from the macroscopic surface normal. (Gale *et al.*, 1977).

APPENDIX E. RATE CONSTANTS FROM NMR

Rate constants for hydrogen adsorption on Ru/SiO₂ catalyst at 296 K (Savargaonkar and King, 1998)

H/Ru _s	0.42	0.63	0.73	0.83
k_a (Pa ⁻¹ s ⁻¹)	6.3×10^5	8.7×10^5	5.7×10^5	1.5×10^5
k_d (s ⁻¹)	4.8×10^2	7.9×10^3	2.1×10^4	2.4×10^4
k_a/k_d at 296 K	1.3×10^3	1.1×10^2	2.7×10^1	6.3×10^0
k_a/k_d at 400 K <i>calculated</i>	9.7×10^{-2}	8.2×10^{-3}	2.0×10^{-3}	4.6×10^{-4}

The apparent rate constants for hydrogen adsorption and desorption were obtained (Savargaonkar and King, 1998) assuming that the adsorption process was Langmuirian with one type of adsorption sites. The rate constants, themselves, were estimated from selective excitation NMR experiments using the model of Engelke *et al.* (1994).

The ratio of adsorption and desorption rate constants at 400 K can be estimated from its value at 296 K. With an increase in temperature the adsorption rate constant is expected to remain constant as it is a non-activated process on transition metals and the effect of temperature on the preexponential factor can be considered small. The desorption rate constant will be a strong function of temperature as it is an activated process. The activation barrier can be assumed to be about 90 kJ/mol from the microcalorimetry data (Narayan, 1998). The preexponential factors, as before,

can be assumed to remain constant when the temperature is increased to 400 K from 296 K.

$$\frac{k_{d\ 296K}}{k_{d\ 400K}} = \frac{\exp\left(-\frac{9000}{296R}\right)}{\exp\left(-\frac{90000}{400R}\right)} = 7.4 \times 10^{-5}.$$

Using the above expression, the ratio of adsorption and desorption rate constants at 400 K were estimated. The calculated values are listed in the last row of the above table. The values corresponding to the hydrogen coverage, H/Ru_s, of 0.63 and 0.73 are comparable to the ratio of k_{abs} and k_{dbs} obtained in the portal model of hydrogen adsorption on Ru/SiO₂.

APPENDIX F. ESTIMATION OF ORDER OF HYDROGENOLYSIS REACTION

Ethane Hydrogenolysis on Ru/SiO₂

The rate of ethane hydrogenolysis reaction was derived as:

$$\text{Rate} = \frac{kK_{E1}K_{E2}P_E}{(K_H P_H)^{\frac{n+1}{2}} (1 + \sqrt{K_H P_H})}$$

When the above equation is considered for the case in which Ru-Ag bimetallic catalyst is used, one of the factors in the denominator becomes close to unity. That term is $(1 + \sqrt{K_H P_H})$. This simplification makes it easy to assign an order of reaction with respect to hydrogen. However, when Ru/SiO₂ catalyst is used, such simplification is not applicable. The value of $\sqrt{K_H P_H}$ at 400 K was determined to be 1.8 from the portal model of hydrogen adsorption when the partial pressure of hydrogen was 585 Torr. The ethane hydrogenolysis reaction was carried out at temperatures greater than 500 K. At 500 K, the value of $\sqrt{K_H P_H}$ is expected to be less than 1.8 but still $\sqrt{K_H P_H}$ may not be far less than 1.

When both the terms are comparable to each other, the following analysis can be applied for estimating the order of reaction with respect to hydrogen:

$$(K_H P_H)^{\frac{n+1}{2}} (1 + \sqrt{K_H P_H}) = (K_H P_H)^{\frac{n+1}{2}} + (K_H P_H)^{\frac{n+2}{2}}$$

$$(K_H P_H)^{\frac{n+1}{2}} + (K_H P_H)^{\frac{n+2}{2}} = 2(K_H P_H)^{\frac{n+y}{2}}$$

where $1 \leq y \leq 2$.

The magnitude of y will depend on the value of $K_H P_H$. The relation between $K_H P_H$ and y is shown in Figure F-1 on the next page. It can be seen that the value of y lies close to 1.5 over a large range of $K_H P_H$.

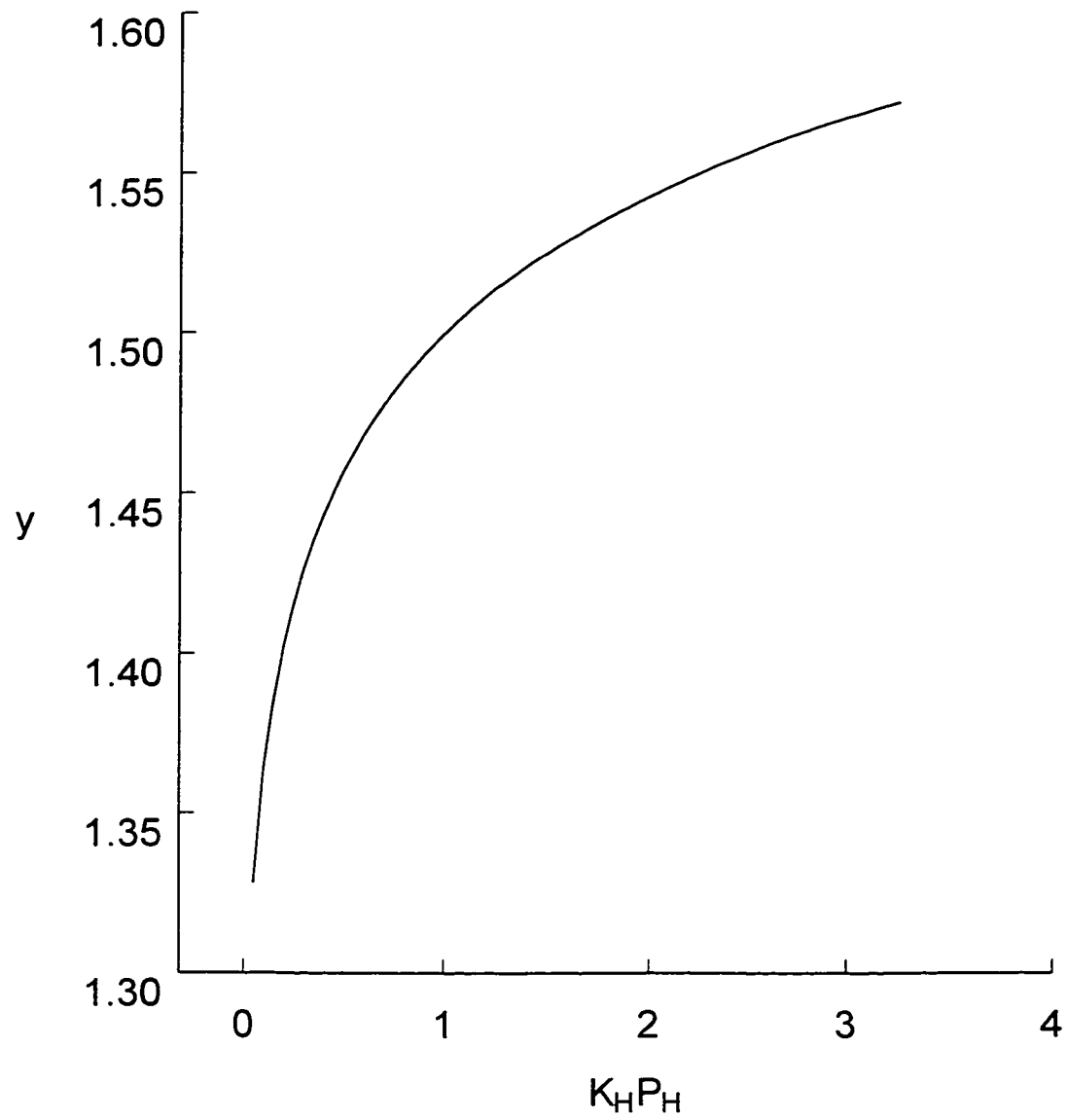


Figure F-1: Variation of y with a change in the magnitude of $K_H P_H$.

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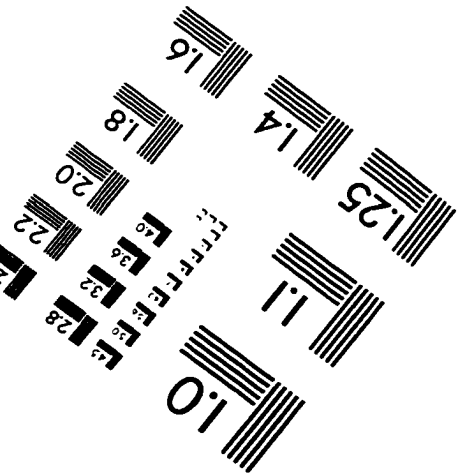
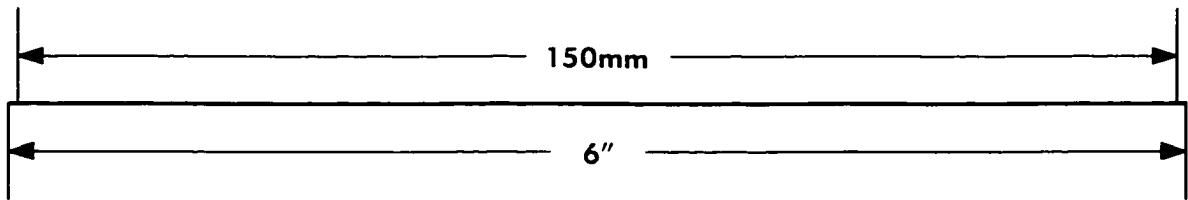
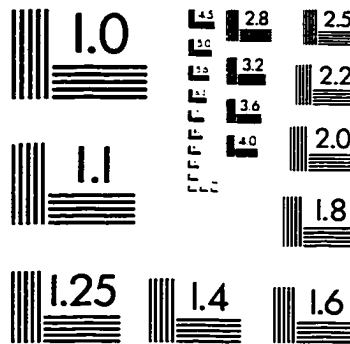
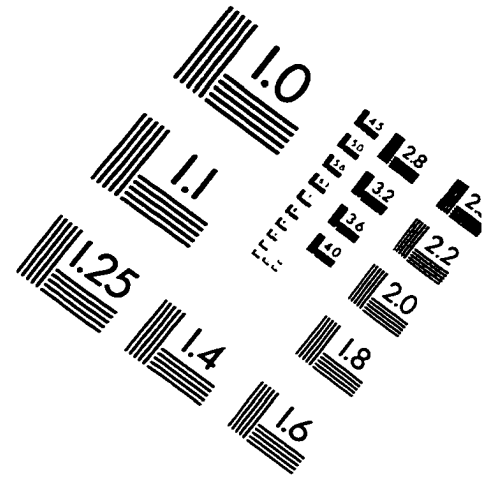
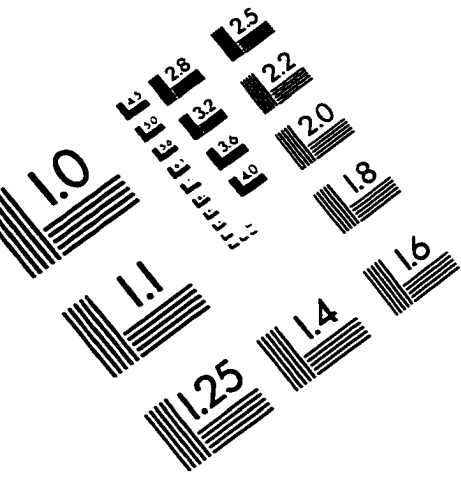
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IMAGE EVALUATION TEST TARGET (QA-3)



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